the glass industry

VOLUME 39, NUMBER 3, MARCH, 1958

# Use of Sulfates in Glass

By W. H. MANRING and R. W. HOPKINS,
Glass Technicians, Inc., Hamilton, Ohio

## INTRODUCTION

• ONE OF THE MAIN FUNCTIONS of sulfates in a glass batch is to control scum formation in the furnace during the melting process. The other major function of sulfates is to promote more rapid fining of the glass and to control oxidation-reduction influences. Where glass fining problems stop and oxidation-reduction problems begin cannot be defined. In most cases glass fining revolve about the state of oxidation of sulfur. J. W. Wright[1] summarizes the problem as follows: "The guess is that undecomposed sulfates or sulfides present within the molten glass are our principal source of troubles in so far as seeds are concerned."

The use of sulfates in glass from our point of view, then, can best be described as the study of the oxidation-reduction influences during the batch melting process. The melting process itself tends to be reducing in nature, with reducing effects being brought about largely by sulfur, sulfides, either from batch or through formation of these compounds due to influence of furnace atmosphere.

Generally sulfates are added to control these natural reducing factors and to aid in the more rapid removal of seed and blisters from the glass. The position of sulfates in accelerating the fining action of the glass melting process is open to a great deal of question. One school of thought, particularly on flint glasses, openly proclaims that sulfates are of no value to fining and are even detrimental. The other maintains that the judicious use of sulfates results in more rapid fining with lower over-all furnace temperatures, plus important physical advantages to glass properties. We hold to the latter theory and believe effective fining advantages are gained through use of sulfates.

It is not our intention to try to resolve this argument as such. Rather, we will present an approach whereby the problem can be viewed more objectively. This work involves a brief discussion of sulfate usage in flint, amber and green glasses plus an empirical method of calculating an oxidation-reduction number for any given glass batch.

Before beginning the discussion, it might he helpful to define our interpretation of an oxidized glass as compared with a reduced glass.

| | | Flint | Amber |
|---|---|---|---|
| | $SiO^2$ | 72.00 per cent | 72.20 per cent |
| | $Al^2O^3$ | 2.00 | 2.00 |
| | $Fe^2O^3$ | 0.05 | 0.20 |
| | CaO | 8.65 | 8.64 |
| | MgO | 2.50 | 2.50 |
| | $Na^2O$ | 14.10 | 14.10 |
| | $K^2O$ | 0.40 | 0.02 |
| | MnO | 0.00 | 0.20 |
| | $F^2$ | 0.10 | 0.10 |
| (Sulfide) | $S^=$ | 0.00 | 0.03 |
| | $SO^3$ | 0.20 | 0.01 |
| | | 100.00 per cent | 100.00 per cent |

In the colorless oxidized glass, the sulfur has been completely converted to $SO^3$, in the reduced glass there is a measurable amount of reduced sulfide sulfur ($S^=$) with only very small amounts of oxidized sulfate sulfur.

## GENERAL DISCUSSION OF THE USE OF SULFATES IN GLASS

### A. Flint or Oxidized Glasses

In reviewing the use of sulfates in flint glass, we find two opposing factors: we must accelerate fining and decolorize the glass at the same time.

Sulfates are specific oxidants for any reducing influences present. In its role of oxidant the sulfate charge will naturally oxidize the selenium metal added to mask the iron color present in the finished glass. One of the

Presented at the Eighteenth Conference on Glass Problems, University of Illinois, Urbana, Illinois, December 5 and 6, 1957.

**TABLE I**

**Oxidation-Reduction Chart**

All values in terms of ozs. of carbon
per 2000 lb. sand batch

| Oxidizing | | Reducing | |
|---|---|---|---|
| 1 lb. Sodium Sulfate ($Na^2SO^4$) | = +0.67 | 1 lb. Carbon (C) | = –16.0 |
| 1 lb. Gypsum ($CaSO^4 \cdot 2H^2O$) | = +0.56 | 1 lb. Sulfur (S) | = – 6.4 |
| 1 lb. Barytes ($BaSO^4$) | = +0.40 | 1 lb. Calcium Sulfide (CaS) | = – 4.0 |
| 1 lb. Nitre ($NaNO^2$) | = +0.32 | 1 lb. Ferrous Sulfide (FeS) | = – 3.3 |
| | | 1 lb. Iron Pyrites ($FeS^2$) | = – 3.5 |
| | | 1 lb. Iron Chromite ($FeCrO^3$) | = – 1.0 |
| 24 lb. salt cake = 1 lb. carbon | | 24 X .67 = 16.0 | |
| 28½ lb. gypsum = 1 lb. carbon | | 28½ X .56 = 16.0 | |
| 40 lb. barytes = 1 lb. carbon | | 40 X .40 = 16.0 | |
| 50 lb. nitre = 1 lb. carbon? | | 50 X .32 = 16.0 | |

most important factors in selenium conservation is the proper balance of sulfate with furnace atmosphere so that excess sulfate does not nullify selenium. Too low a sulfate charge will decrease selenium consumption but may result in more susceptibility of the glass to higher seed and blister count. Net result in some cases of low sulfur usage will find furnace operating temperature becoming higher and higher. What little money has been saved on selenium or improved decolorizing has gone by the board through increased melting costs. A typical question from management at this point is: "Why do we have to run this furnace so hot?"

By these statements we do not mean to imply that sulfates are the only medium whereby the fining process can be accelerated. Furnace design, obtaining proper glass flaw, grain size of raw materials, wetting of batch to reduce segregation, and many others are very definite and real factors in the over-all problem. Sulfates do, however, have their place in this problem of melting and fining of oxidized flint glasses.

### B. Amber or Reduced Type Glasses

It has been said of this type of glass that the normal fining agents such as sulfates cannot be used because they destroy color. This is not a true statement of fact. Sulfates are usable in this type of glass and are in effect quite necessary in order to develop the stability necessary for modern high pull rates.

Stabilization of amber glasses in so far as seed and blisters are concerned is accomplished by the direct use of sulfates to destroy the unstable type sulfide color former.[2] Color thus destroyed is replaced by the increased use of either iron sulfide (FeS) or iron pyrites ($FeS^2$) which are comparatively quite stable. Stating the problem in another way, "amber glasses having higher iron level tend to be more stable than those of low iron content." Higher iron in finished glass is accomplished by adding both sulfate and stable iron sulfide colorant.

One of the pleasing peculiarities of an amber glass stabilized in this manner is the fact that it possesses the characteristic of rarely having load seed as such. The usual pattern is that as furnace temperature is gradually decreased, batch stones begin to appear before seeds and blisters become a real problem.

### C. Emerald Green Glasses, or Glasses Colored With Iron Chromite

Emerald green glasses, as we view the problem of sulfate usage or oxidation-reduction, lie somewhere in between an oxidized flint and a reduced amber. If we over-oxidize this type of glass, a yellow discoloration results from the development of too much ferric iron and perhaps some chrome oxidation. If we over-reduce this type of glass, amber or sulfide development creates a yellow amber type of discoloration which is equally non-acceptable. This type of glass demands a melting equilibrium which will be almost neutral, to maintain the iron and chrome components in their lower state of valence.

Ordinarily, in this situation, it would normally be felt that again the advantage of sulfates would be too dangerous in the melting of this type of glass. However, this is not true since sulfates can improve the melting and fining rate simply by adding the proper amount of reducing agent in form sulfur, sulfides or even carbon. This is the same principle that is involved in the melting of plate or window glass compositions wherein carbon is added to accelerate the decomposition of the salt cake ($Na^2SO^4$) added to the batch. Whenever cancelling amounts of oxidation and reduction are added, no color change results with the net advantage of increased fining assistance.

## INFLUENCE OF FURNACE ATMOSPHERE ON SULFATE USAGE

Dr. Ralph Day[3] in his book on glass research methods expresses the problem as follows in referring to the theory of fining glass and bubble formation:

> "There is also the effect of the oxidation-reduction state of the glass melt, of the atmosphere above the melt, and of the container itself. It is known that $CO^2$ and $H^2O$ are more soluble in glass than are the reduced gases $H^2$ and CO. The reaction of the former with any chemically reducing materials may therefore be an important cause of seedy glass. Are amber glasses less seedy because this reaction has removed the super-saturated gas 'pressure' in the hot end of the furnace?"

In effect the fining of glass has to do with oxidation-

**TABLE II**

**Emerald Green Glasses**

Batch and Oxidation—Reduction Data

| Glass Number | # 1 | # 2 | # 3 | # 4 | # 5 | # 6 |
|---|---|---|---|---|---|---|
| Sand | 2000 lb. | 2000 lb. | 2000 lb. | 2000 lb. | 2000 lb. | 2000 lb. |
| Soda Ash | 740 | 751 | 762 | 762 | 762 | 762 |
| Burn't Lime | 260 | 260 | 260 | 260 | 260 | 260 |
| Calumite | 130 | 130 | 130 | 130 | 130 | 130 |
| Nepheline Syenite | 120 | 120 | 120 | 120 | 120 | 120 |
| Iron Chromite | 15 | 15 | 15 | 15 | 15 | 15 |
| Fluorspar | 30 | 30 | 30 | 30 | 30 | 30 |
| Barytes | 30 | 30 | 30 | 30 | 30 | 30 |
| Salt Cake | 30 | 15 | 0 | 0 | 0 | 0 |
| Carbon | 0 | 0 | 0 | 16 oz. | 32 oz. | 48 oz. |
| Reducing from: | | | | | | |
| Calumite = | −11.7 | −11.7 | −11.7 | −11.7 | −11.7 | −11.7 |
| Chromite = | −15.0 | −15.0 | −15.0 | −15.0 | −15.0 | −15.0 |
| Carbon = | 00.0 | 00.0 | 00.0 | −16.0 | −32.0 | −48.0 |
| Total Reducing = | −26.7 | −26.7 | −26.7 | −42.7 | −58.7 | −74.7 |
| Oxidizing from: | | | | | | |
| Barytes = | +12.0 | +12.0 | +12.0 | +12.0 | +12.0 | +12.0 |
| Salt Cake = | +20.0 | +10.0 | 00.0 | 00.0 | 00.0 | 00.0 |
| Total Oxidizing = | +32.0 | +22.0 | +12.0 | +12.0 | +12.0 | +12.0 |
| Oxidation | +32.0 | +22.0 | +12.0 | +12.0 | +12.0 | +12.0 |
| Reduction | −26.7 | −26.7 | −26.7 | −42.7 | −58.7 | −74.7 |
| Number | + 5.3 | − 4.7 | −14.7 | −30.7 | −46.7 | −62.7 |
| Color | Pale Yellow Green | Pale Yellow Green | Slight Yellow Tint to Green | Normal Blue Green | Deep Blue Green | Amber Tinted Dark Green |

reduction level of glass proper, furnace atmosphere, and finally with furnace refractories.

With regard to furnace atmosphere, this point cannot be emphasized too strongly. Each melting unit is an individual in its own right and even this individual unit will change appreciably as the checkers begin to slag over or clog up. The empirical approach to be described later is valueless unless it is readjusted to the furnace atmosphere in question.

In a producer gas atmosphere sulfate usage is markedly increased over other fuels, the order or magnitude of this increase for comparative purposes being 15 to 20 lb. or higher of gypsum per 2000 lb. sand over normal usage. Highly oxidizing oil firing requires less than normal amounts while natural gas firing depends largely upon the type of firing and the amount of excess combustion air being used. It is the atmosphere immediately above the batch piles as they move out into the furnace that counts rather than flue gas analysis taken at any given point. The answer to the question of how much sulfate should be used in any given glass batch is not a simple one; it requires considerable thought plus some trial and error. Extreme conditions can be illustrated by the following equations:

1. $2Na^2SO^4 + C \ldots\ldots 2Na^2O + 2SO^2 + CO^2$
2. $2Na^2SO^4 + CO \ldots\ldots Na^2O + SO^2 + CO^2$

## AN EMPIRICAL APPROACH TO EVALUATING OXIDATION-REDUCTION INFLUENCES

### A. Explanation of Factors

In order to simplify the task of determining optimum quantities of sulfate in a glass batch, this work relies on mathematics to establish a yardstick or measuring device. Oxidized glasses will carry plus values whereas reduced glasses will show as minus quantities. Under this type of system an oxidized glass will normally have a range of –1.0 to +15.0, amber glass will have a range of –15.0 to –40.0, emerald green glasses range from –12.0 to +2.0, depending upon type of furnace atmosphere.

The approach involves assigning values for oxidants such as salt cake ($Na^2SO^4$), gypsum ($CaSO^4 \cdot 2H^2O$), and barytes ($BaSO^4$), in terms of carbon as the standard. By definition 1 oz. of carbon per 2000 lb. sand batch has a reducing value of –1.0. Basis for assigning these values are both practical experience and written equations similar to the following:

$3\ Na^2SO^4 + CaS \rightarrow 3Na^2O + CaO + 4SO^2\uparrow$

6 lb. salt cake = 1 lb. calcium sulfide

$3\ CaSO^4 \cdot 2H^2O + CaS \rightarrow 4\ CaO + 2\ H^2O + 4SO^2\uparrow$

7.2 lb. gypsum = 1 lb. calcium sulfide

$3\ BaSO^4 + CaS \rightarrow 3\ BaO + CaO + 4\ SO^2\uparrow$

10.0 lb. barytes = 1 lb. calcium sulfide

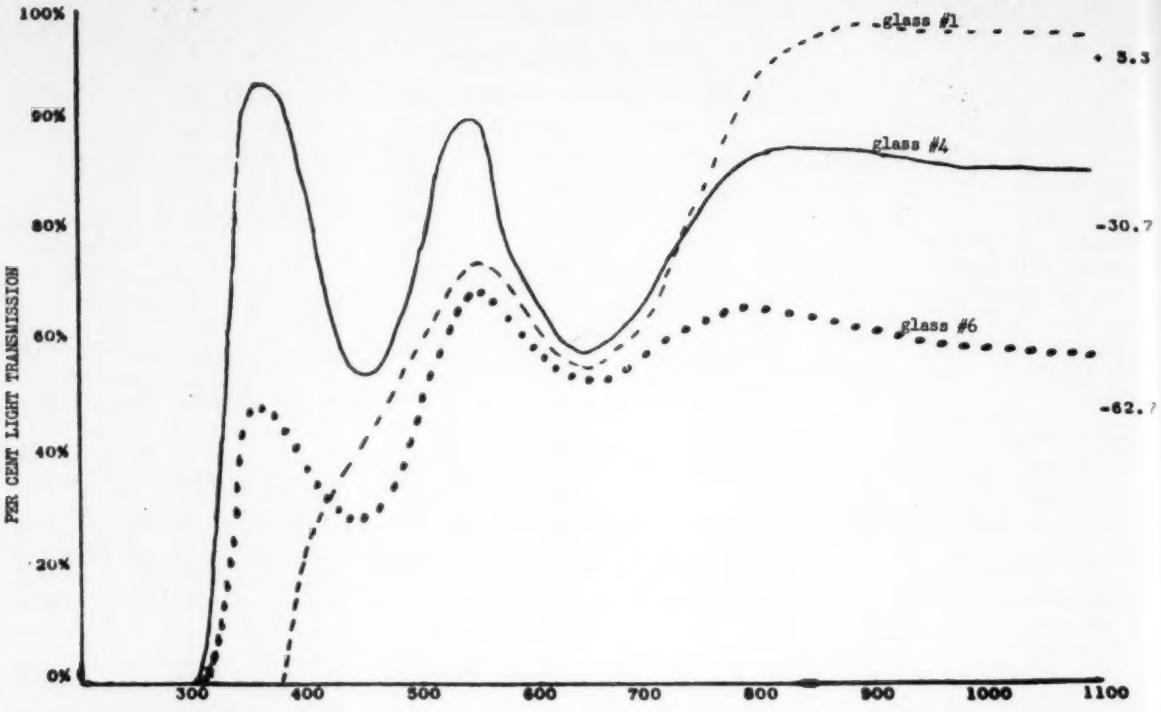



**Fig. 1. Spectrophotometric curves on glasses #1, #4 and #6.**

**Wave length Mu has been corrected to standard width 2.0 mm.**

These equations, incidentally, tell the story rather well of the relative values of these various sulfates in so far as oxidation-reduction problems are concerned. Table I shows the values assigned to various batch ingredients.

An approach of this type cannot be exact; factors in some cases can only be obtained through practical experience. The basic equation involved is the reaction between salt cake and carbon and is strictly theoretical. Nitre for example, in our experience, loses its oxygen so rapidly that full theoretical value cannot be utilized, this loss taking place before sulfur is oxidized. Another factor which at first glance appears to be in error is the one for iron pyrites. Our experience with iron pyrites as a colorant is that in a properly stabilized amber its influence is almost identical with ferrous sulfide. Apparently in normal oxidizing furnace atmospheres iron pyrites loses the one molecule of sulfur at very low temperatures and at a very rapid rate, becoming in effect FeS for all practical purposes. Furnace atmosphere is always an important influence and modified to fit the melting unit in question. Arsenic is conspicuous in its absence from the table, largely because it first is a reducing agent, later an oxidizing agent, normally being used in conjunction with nitre.

### B. Application of Factors to a Specific Problem

Listed in Table 2 is complete batch data on six emerald green glasses illustrating how these empirical factors may be applied. Reduction value from Calumite as a raw material is obtained by converting total sulfur value to calcium sulfide which is the form of sulfur occurrence in this material.

The six glasses illustrate the range from over-oxidized to over-reduced chromite green colors. Color control over emerald green glasses is almost solely dependent upon the oxidation-reduction balance of the glass melt and is a very real problem in the production of this type of glass. In this particular example the operating range happens to be from about –25.0 to –50.0 for desired color. In so far as furnace atmosphere is concerned on this specific problem it indicates the melting unit was highly oxidizing.

As a further check on the properties of these glasses, complete spectrophotometric curves were run on a Beckman DU. Three of these curves are shown in Fig. 1; these represent the extreme oxidized glass #1, normal color #4, and the reduced glass #6. Interpretation of the curves show marked differences in iron valence at 1100 millimicrons. Reduced glass #6 shows amber type characteristics in the ultra violet. Oxidized glass shows a sharp cut off around 400 Mu.

### PROPERTIES OF A GOOD SULFATE

1. It will tend to decompose before melting.
2. Decomposition will take place over a temperature range in which rapid oxidation and fining can take place.
3. A large amount of $SO^2$ for fining purposes and $O^2$ for oxidation purposes will be provided.
4. Excessive segregation to the melt surface will not occur during the glass preparation process.
5. It will be adaptable to efficient shipping, storage and handling.
6. It will give maximum over-all benefit at a reasonable cost.

(*Continued on page* 170)

# Glass: Its Transparency and Structure

## Part II. Transparent Colors, Surface and Optical Effects, Presence of Particles, and Transparency

By H. H. HOLSCHER, Technical Assistant
to Director of Research, Owens-Illinois Glass Company, Toledo, Ohio

**TABLE OF CONTENTS**

5. Partial Light Absorption or Development of Transparent Colors

*One Reason for Transparent Colors*

6. Surface Effects
   - 6.1. Index of Refraction
   - 6.2. Invisible Surfaces

7. Concept of Particle Size and Visibility
   - 7.1. Visibility in Detail
   - 7.2. Visibility by Light Scattering and Location
   - 7.3. Light and Color Effects from Invisible Particles
   - 7.4. Question of Magnification and Wave Lengths Used for Viewing
   - 7.5. Summary

*Absence or Presence of Light-Scattering Particles and of Internal Surfaces*

8. Particles in Gases, Liquids and Solids (Including Glasses)
   - 8.1. Particles in Gases
   - 8.2. Particles in Liquids
   - 8.3. Particles in Solids
   - 8.4. Summary

*Homogeneity*

Appendix

### 5. PARTIAL LIGHT ABSORPTION OR DEVELOPMENT OF TRANSPARENT COLORS

(Based largely on References 6, 13, 30, 40 and 41)

Elements such as copper, cobalt, chromium, iron, nickel, manganese, etc., produce deeply colored glasses when present in solution in the glass. Such colored glasses generally also possess some transparency. They exhibit partial light absorption in restricted portions of the spectrum. They possess no light-scattering properties (see Section 8). The exact reasons (from the atomic structure viewpoint) for these transparent colors are not known. Weyl (Ref. 5, p. 1-9) discusses relationships to valence, valence change, polarization effect, chemical nature, electrical nature, etc. The origin of color is related in some way to a field of force which is not fully saturated or balanced. The problem is even more complicated theoretically when a compound rather than an element is involved. Nature of bonding of the compound, as well as the chemical and electrical properties of the component elements, enter into the discussion of the color effects obtained. One major factor from this color viewpoint is the dependence upon the outer electron field. Later Weyl (Ref. 5, p. 366) states, "In earlier parts of this monograph, the absorption of light was treated as due to the result of electronic jumps. In the ions of the transition group it was assumed that a valency electron was shifted into a higher orbit. The sharp absorption bands . . . . of rare-earth ions were explained by electronic transitions taking place in inner protected orbits. The blue color of iron glasses containing both divalent and trivalent ions . . . . were interpreted as an electronic transition involving two ions of the same element but different valency."

Regardless of theoretical explanations, there are very interesting relationships between color and position within the Periodic Table (Table 1). For instance, a Biltz rule for color is quoted as follows (Ref. 13 and Ref. 5): "Complete saturation of the chemical or electrical valency, as well as strong binding forces, favor light transmission. Unsaturated valences or weak bonds favor absorption and deeper color."

We can take a colorless liquid and make it colored by the addition of certain elements to it. A solution of copper sulfate is blue because of the presence of copper ions. A solution containing chromium salts may be green because of the presence of chromium ions.

(References 40 and 41) These same effects carry through to the colors of the elements and the colors of various salts. For instance, elements with atomic numbers 1 to 21 are colorless. Elements in the range from 22 to 29 are colored, at least in certain states of valency. This group includes titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper. We then note that elements with atomic numbers 30 to 40 are colorless, 41 to 46 are colored, 47 to 56 are colorless, etc. The locations of these elements (in relation to color) in the Periodic Table is an interesting study. (See Section 4.1.) In other words, in the Periodic Table:

a. Color develops as the atomic weight increases.
b. Neither the strongly positive nor the strongly negative elements show much color.
c. Color development reaches a maximum in the eighth group.
d. There is a tendency for development of deep color in the middle of the first double period, and to a lesser degree in the middle of the other long periods.

We are particularly interested in the group of transitional elements which are those elements that have coloring ions at some valences and colorless at others.

Such transitional elements include titanium, vanadium, copper, silver, cerium, etc. Elements with ions that are commonly coloring include chromium, manganese, iron, cobalt, nickel, platinum, gold, and some of the rare earths. In each of these cases, there are vacancies in the outer orbits.

It is thus apparent that the development of coloring ions comes from certain types of electron excitation. This is again a case where the electrical properties of the free ions interfere with the wave in an electromagnetic fashion. A good illustration is the use of iron oxide in glass, with the ferric iron giving yellow color, the ferrous iron giving blue color, and the combination in general giving a green-colored glass. In the case of the gold ruby we have actual metal present in the colloidal state and the color is due to the combination of the size of the metal particles present plus the absorption characteristics of the metal.

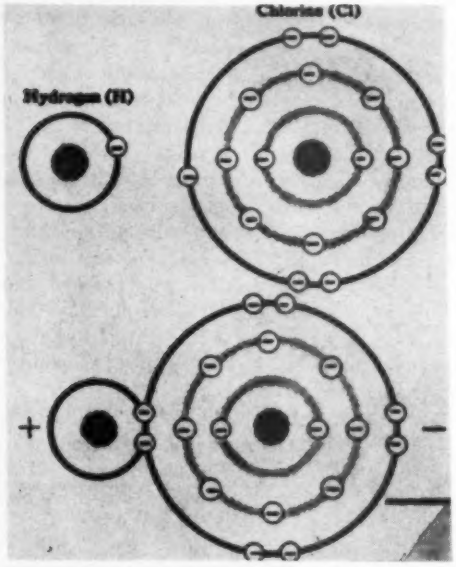



**Fig. 10. Polar groups. A polar bond has characteristics of both covalent and ionic bonds. In the formation of the hydrogen-chloride molecule, the chlorine outer shell is completed, but the hydrogen does not tend to give up its electron completely, as happens in an ionic bond. The resultant molecule is polarized, the hydrogen portion being effectively positive, the chlorine end being negative. (Ref. 23)**
From "Fundamentals of Electrical Insulators", J. Swiss and T. W. Dakin, *Westinghouse Engineer, 14* (1954).

These effects are similar to the various spectroscopic and energy releases caused when atoms are excited. There are typical excitation colors for all the atoms, some of which are evident in the visible and some of which are not. Some occur only under high temperature or high energy excitation. We are also acquainted with the fact that certain elements will give colors when they are more highly excited, such as, for instance, when they are heated (for example, sodium yellow color).

(Reference 30) It can generally be said that light absorption in the visible involves the displacement of electrons within a molecule. When the energy of the absorption become fairly great, then the absorption is in the ultraviolet. However, when the masses of the particles involved become greater than electrons, we can have relative motion of charged atomic masses or rotation of polar groups of atoms (Fig. 10). This results in the infrared spectra. Fig 3 gives the general picture of the different types of spectra, wave length ranges, and covers also the energy ranges which cause these absorptions or emissions. The black dots represent electrons, and the larger circles represent atoms in the molecule. We note that when we get rotational motions of polar groups, we are in the far infrared. When we get vibrational motions within the molecule, we are in the near infrared. When we have minor electron jumps such as occur in colored glasses and in valence changes, we are in the visible. Major electronic jumps involve the ultraviolet and X rays. The energy which is involved in these movements varies from a few hundred Calories per mole up to several hundred thousand Calories per mole. Since chemical reactions require from 10,000 to 100,000 or more Calories per mole, the effects of light on such reactions are very pronounced for the short ultraviolet. The long waves (infrared) have no such effect.

### One Reason for Transparent Colors*

Colored transparent glasses are the result of additions of certain coloring ions to glass. These ions are coloring because they possess two or more states of atomic structure, or varying states of the outer orbits which give different valency. In any case there are electronic changes, or varying positions of electrons, which produce energy changes. Energy changes give absorptions of varying wave lengths, thus giving rise to partial light absorption. This results in transparent colors.

## 6. SURFACE EFFECTS

(References 27 and 28) We see glass because we see its surface — specifically its reflection properties. While it is transparent, the surface reflects approximately 4 per cent of the light when the refractive index is near 1.5. Thus with two polished surfaces a clear, colorless glass plate transmits about 92 per cent of the received light. At certain angles we get a very large regular or specular reflection. (See Figure 11.) When the surface is not polished but is roughened or sand blasted, we get diffuse reflection in all directions (Figure 12). If the sand blasting is intense enough to give a white surface, the diffuse light may be a great share of the total light received. The object then becomes white and opalescent and one cannot see detail through it. However, its light transmission may be considerable and shadow effects may be readily perceptible through it. If we put oil on the surface, we may cut the whiteness and give greater visibility through the sheet. One may rub the surface with the oil from one's hand. If we coat the surface with a transparent liquid of the same index of refraction as the glass, we get considerable transparency in the glass sheet.

If you crush glass, you get a white-appearing powder even though each particle is, in itself, transparent. The

*There are other reasons for colored tranparent glass. (See Section 8.)

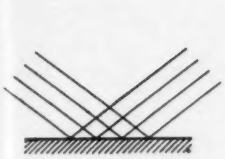


Fig. 11

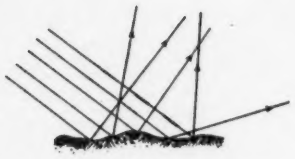


Fig. 12

**Fig. 11. Direct or specular reflection from a relatively large polished surface. (Ref. 28)**
**Fig. 12. Diffuse or irregular reflection from a relatively large but ground or rough surface. (Ref. 28)**
From *Practical Physics*, M. A. White, McGraw-Hill Book Company (1943).

ground glass is thus mixed with air. The effect is similar to smoke in air (Fig. 13) or scattering of light from small particles (Fig. 14).

Now if we pour over the crushed glass a transparent liquid of an index of refraction equal to that of the glass, the glass particles become invisible. We are making the surfaces invisible by matching index of refraction.

## 6.1. Index of Refraction

(Reference 28) The bending, reflection or absorption of light by a mass are the factors which contribute to visibility. If a particle is opaque, we see it because surfaces reflect light. The physical laws of optics cover direct or specular reflection (Fig. 11) (where the angle of incidence equals the angle of reflection) and diffuse reflection (Fig. 12). These apply both to transparent and opaque masses. Absorption involves the receipt of light and not its return (as in a dark metal). It occurs where there are great numbers of electrons free to move and destroy the light by electrical interaction.

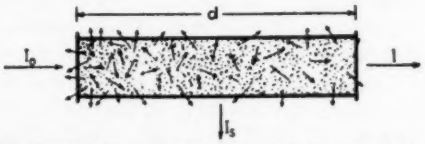



**Fig. 13. Scattering of light by finely divided particles such as those in smoke. (Ref. 27)**
From *Fundamentals of Physical Optics*, F. A. Jenkins and H. E. White, McGraw-Hill Book Company (1937).

If a particular particle or mass is transparent, it is common to state that it has an index of refraction. The index of refraction of a transparent material is the ratio of the speed of light in a vacuum to the speed of light in the material. Actually the speed of light in air is only very, very slightly different from the speed of light in a vacuum, so that it is common to state that the index of refraction is normally related to that of unity for air. The speed of light in air is approximately $3 \times 10^{10}$ cm. per second. It is found that light is bent when it enters an object, at an angle less than 90° to the surface, wherein its speed is decreased. This bending of light is known as refraction (Figs. 15 and 16). This can be most easily demonstrated by putting a straight, long stick into a pond of water at an oblique angle. You will then note that the stick seems to bend at the surface. In the same fashion (Fig. 17) light bends when it passes from water into air at an angle less than 90°.[1]

[1]An interesting usage of the physical optics (bending and total reflection) of glass is given in Appendix 3.

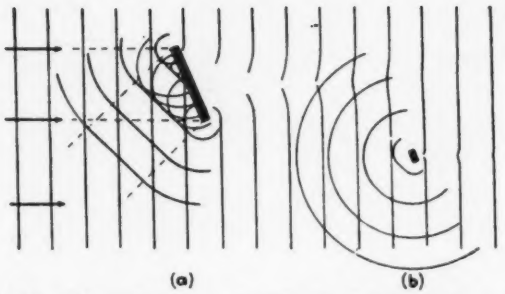



**Fig. 14. The reflection and diffraction of light by small objects comparable in size to the wave length of light. The left diagram represents a case of direct reflection from a particle of size about two times the wave length. The right diagram shows how a particle of size of one-fourth the wave length acts in a light-scattering manner. (Ref. 27)**
From *Fundamentals of Physical Optics*, F. A. Jenkins and H. E. White, McGraw-Hill Book Company (1937).

There are of course, angles where almost total reflection results from transparent surfaces. (See Fig. 17, where one beam reflects back into the water.)

Total reflection occurs at all angles for a mirror, but here the perfect glass surface holds a coating of highly reflective metal (Fig. 18) which reflects the light.

This question of visibility of a particle is related to a change of index of refraction from the particle to the fluid in which it is placed. If you place a particle of glass which has an index of 1.5 in a fluid like monochlorobenzene, which also has an index of 1.5, then you will be unable to see the glass, since both bodies are transparent.

The fact that you cannot see the glass particle is related to the fact that you normally saw only the surface of the glass and now this surface is made invisible by placing around it a fluid which has equal effect on bending of light. In other words, by matching the index of refraction of a solid with a liquid, you can make one or the other invisible. For instance, if you could make a glass with an index of refraction of 1.000, which is that of air, you would find that the glass would be invisible in air. There would be no surface which could be seen. Similarly, in the opposite direction, if you take a clear chunk of glass and grind it up into rather small particles, say of 1 mm. diameter, you will find that these particles take on a white appearance in massive form because the particles are mixed in with air. In other words, we have a system with different indices of refraction and we get

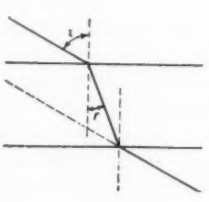


Fig. 15

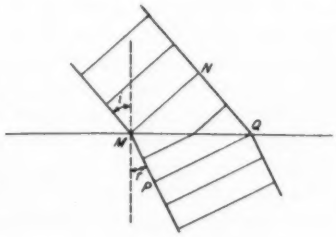



Fig. 16

**Fig. 15. Refraction or bending of light when it enters a transparent object. (Ref. 28)**
**Fig. 16. Change in direction of a beam of light on entering a transparent object. (Ref. 28)**
From *Practical Physics*, M. A. White, McGraw-Hill Book Company (1943).

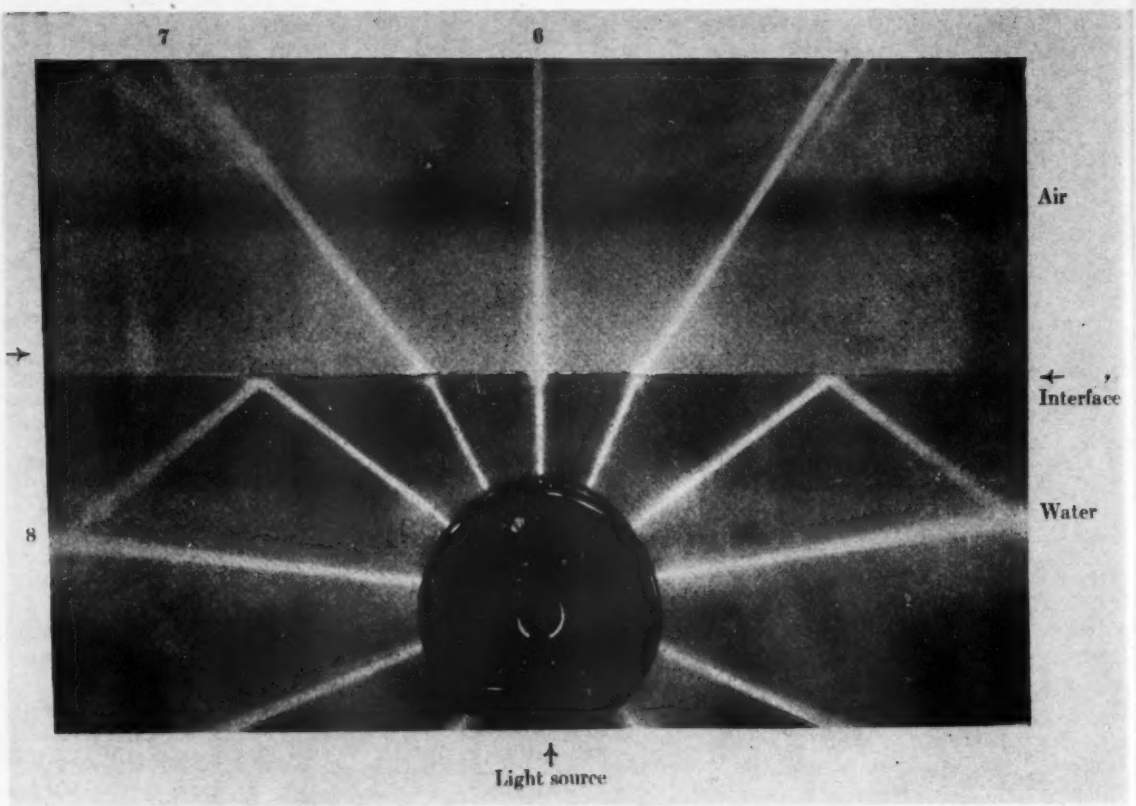



**Fig. 17. Refraction of rays of light from an under-water source to air. Note bending at the water-to-air surface and total reflection from the under-water surface. (Reference noted is 49.)**

From *Analytical Experimental Physics*, M. Ference, H. B. Lemon, and R. J. Stephenson, University of Chicago Press, 2nd ed. (1956).

whiteness or opacity due to this difference, even though both the air and the particles themselves are in massive volume transparent. This, then, covers one of the main properties of materials which cause visibility. This is their capacity to deflect or bend or refract the light waves we use for viewing them.

### 6.2. Invisible Surfaces

(Reference 48) It has been mentioned above that surfaces can be made invisible by having no change of index of refraction—for instance, a glass article immersed in monochlorobenzene. In order to avoid any misunderstanding, it is perhaps wise to include here another method which, while it doesn't make a surface totally invisible, does overcome some of the reflection properties of surfaces. You all know that a glass surface has a high reflection and objects can be seen by this reflection. You have undoubtedly heard also that there are methods of coating glass surfaces which largely eliminate this reflection. These methods of producing antireflection coatings are based on optical interference of waves which are received and reflected from the surface. We can produce direct interference of light waves by having one crest of a wave counteracted by one valley of another wave. This then tends to optically produce invisibility. The antireflection coatings placed on glass surfaces are coatings of a specific index of refraction, related to a specific thickness of that coating, which together produce nearly total interference of waves. The surface therefore does not have its normal light reflection value of 4 per cent, but the light becomes almost totally transmitted through the surface. The essential point to remember here is that this is an optical effect produced by index changes and thickness on the surface of glass. These coatings are used largely in optical components (lenses, etc.).

The invisible display window works on the principle of throwing the reflection to where it is not visible. The curved glass reflects downward, where reflection is absorbed in the architecture of the unit.

## 7. CONCEPT OF PARTICLE SIZE AND VISIBILITY

Unless particles or objects are within certain physical size ranges, we may not be visibly aware of their presence. We can breathe air, but we do not see it. Moisture can be in the atmosphere, but we do not normally see it. When it does become visible as fog, we know that this is due to moisture present in larger particle sizes. We are aware of smoke because of certain effects it has on light.

Once again, these are illustrative of mixtures of gases and particles in which one of several explanations is appropriate. For convenience, we may divide the effects into:

a. Visible in detail.
b. Location visible by light-scattering effects.
c. Light and color effects from normally invisible particles.

In the larger particles, we have index of refraction effects, but these effects become less usable as the particle size becomes smaller.

### 7.1. Visibility in Detail

(Based largely on References 6, 29, 30, and 31) At night, when an automobile approaches, the first effect is that of seeing a single light. As the car gets closer, the one light becomes two and you see them both. At this particular instant, the resolving power of the eye is effective in splitting the one beam into two.

The above effect enters into the separation of one particle from another. If the particles are very fine, then the eye can see two particles if they are separated approximately .02 cm. or .008 inch, and if they are viewed at 25 cm. distance from the eye. The fundamental relationship is really one in which the two particles have a certain angle between them when lines from each particle are drawn to the point of the eye. This angle is approximately 1/20 of a degree. Thus distinction into two depends directly on distance from the eye. This is the case of the automobile headlights.

The same concept covers the perception of difference in appearance along a single object—for instance, the comparison of physical characteristics from one end of an object to the other. This we can call the limit of seeing detail on a single particle. In other words, if we wish to actually determine appearance, we must bring the dimensions up to this realm of .02 cm. in size.

We can, of course, do this by optical magnification. (See Section 7.4.) The best light magnification is approximately 1000 diameters, or 1000 magnification, and thus we could expect to study particles of about .02 cm. divided by 1000 or .00002 cm. size. Actually we are limited to about .00004 cm. or 4000 Å. in practice (Table 3) under best magnification. Plain counting may be possible to 2000 Å. (See Appendix 1.)

### 7.2. Visibility by Light Scattering and Location

(Based largely on References 26, 27, 31, and 32) The particle which is visible in detail (Section 7.1) has a dimension under best light magnification of approximately 4000 Å. This dimension is of the same order of magnitude as the wave length of the shortest of the visible violet range (Table 3). In this kind of a situation the particle has a surface of dimension comparable to the dimension of the wave length of light. In Fig. 14a, the surface reflects the light and produces actual reflection.

This case can be contrasted with Fig. 14b, where the particle is about 1/4 the dimension of the wave length. Here we produce an effect which is similar to a point source. The wave reflected or refracted does not stay flat but scatters in all directions. This light scattering causes the particle location to be visible, but details of surface are not resolved.

Fine dust particles may be in a room but be distinctly visible only when a beam of sunlight passes through the air and at the same time you look at the light at an oblique angle. Here the dust acts as a scatterer of light and you plainly see the particles of dust. This same effect is noticeable for some forms of smoke particles (Fig. 13).

Turbidity is evident when the particles are sufficiently concentrated within a medium of average dimension (say 1/4″ to 1″ thick) and when the particle sizes are in the realm of 1000 Å or so. The effect becomes greater as the particle size increases and is very prominent in the realm of 2000 to 100,000 Å and larger. It is estimated that single particles within the size realm of 10,000 to 100,000 Å, more or less, can be located by the eye without magnification. Fumes are visible in air, and their size range is from approximately 1000 to 10,000 Å. They represent a fair concentration of particles. Dusts range to somewhat larger sizes.

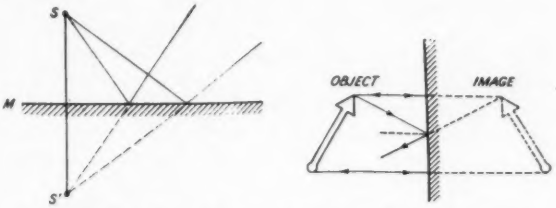



**Fig. 18. The reflection from a plane mirror is shown on the left diagram. The image formed by a plane mirror is illustrated on the right diagram. (Ref. 28)**
From *Practical Physics*, M. A. White, McGraw-Hill Book Company (1943).

The ultra-microscope, which uses oblique illumination, is claimed to be useful down to approximately 40 Å particles when the latter have high index of refraction.

Thus light scattering, combined with particle location, is a useful tool within the intermediate size ranges of particles. Research of this type is commonly done within the range of a few hundred to several thousand Å.

### 7.3. Light and Color Effects from Invisible Particles

(This section is based largely on References 6, 25, 27, 31, 32, 49, 53, 54 and 55) There are effects which are visible as light or color from particles of such small dimension that locations by spots of light are not shown. This is also known as a scattering and is broadly explained as an interaction between the very slight electromagnetic field surrounding the particle with the electrical components of the light. However, the effect is better visualized as a change of density or presence of an inhomogeneity in the molecules or at the molecular dimension. While we cannot apply directly the "index of refraction" concept in which a definite surface must exist, we can carry the mechanical picture down to molecular dimensions. When thinking of gases we can accept them as mixtures of molecules within a vacuum. It all depends upon the fundamental unit of measurement one is using. Inhomogeneity at the molecular level is a simple concept of change in concentration of electrons. The latter in effect is what causes optical inhomogeneity. In fact, the concentration of electrons in glass is the primary delaying or bending medium which results in an actual index of refraction.

The scattering of light by very small particles was early known as Rayleigh scattering. However, this term now covers two more or less different phenomena. Some authorities confine the term to a very weak and almost invisible scattering phenomenon related directly to the

electrical nature and not to particle size. However, the interpretation of Rayleigh scattering of most interest to us is related to particle size. The scattering is evident down to about 1/20 of the wave length of the light used. For visible light this would reach down to about 150 Å.

Since we do not see spots of light in Rayleigh scattering, just what effects are visible? The first is one of color. The mathematical basis for Rayleigh scattering is one where the wave length of light enters into the equation. The scattering effect is greater as the wave length of light decreases. For a difference of wave length in the two extremes of visible light—that is, blue at 4000 Å and red at 7600 Å—the scattering is ten times as intense in the blue as in the red. Thus tobacco smoke appears blue. Smoke is in the range of particle dimension of .00003 cm. to .0000001 cm., or from 10 Å to 3000 Å. (It must not be inferred that all smoke has no particles visible by location. In many industrial operations smoke carries free carbon particles due to incomplete combustion.) Fig. 13 gives the scattering effect of smoke. The blue color of tobacco smoke is a selective scattering by wave length.

In the atmosphere, where we can see miles of thickness —toward the sky—we get a selective scattering from the molecules and aggregates of molecules. While their particle dimensions may not approach the 150 to 200 Å of some other cases, the thickness of some miles gives a blue sky.

The sunset is red because of some related effects. The blue light of the horizon sun is scattered, leaving the red. The blue light is also diffracted more than the red by the earth's atmosphere and bent out of the field of vision. In addition, the atmosphere close to the earth contains more dust particles, and we look through a greater thickness of this layer toward the setting sun. Dust particles—being larger—tend to color the sunset red by diffraction effects.

### 7.4 Question of Magnification and Wave Lengths Used for Viewing

(Reference 6) In the cases of particle effects discussed in Section 7.3, we have made some reference to wave lengths. It is apparent that the various effects are related to the particle size and the wave length.

For instance, the light microscope can resolve particles down to about the wave length of light used for viewing:

For ordinary light, we resolve 4000 Å size.

For ultraviolet light, we resolve 2000 Å size.

Now we progress to the reason for use of the electron microscope. In this instrument we do not use visible light, but rather beams of electrons. These electrons have wave properties, and the wave lengths are much shorter than visible. (Visible is 4000-7000 Å wave length. See Table 3.) By proper procedure the effective wave lengths of the electrons used may be made as low as 1 Å unit. Now since this is 4000 times as short as the shortest of the visible violet range, we should be able to see particles 4000 times as small. Actually the limit of resolution of the electron microscope is not 1 Å, but nearer 20 to 40 Å. Much rough work with it is done in the range of 40 to 200 Å units. The electron beam is made visible by a fluorescent screen.

X rays are useful because they have a wave length which falls near the distances between molecular centers in solid or liquid materials. While we cannot see directly the patterns of positions of such centers, we can study them by using X rays of wave lengths from 1 to 100 Å. Note in Table 3 that atoms and molecules and X ray wave lengths fall within the same realm of dimensions.

Rayleigh scattering is studied in different realms of dimensions by using different wave lengths:

Using light — down to approximately 150 Å particles.

Using X rays — " " " atomic and molecular sizes.

(See Table 3.)

In wave reflection, the particles must be separated by distance similar to the wave length used (Fig. 19).

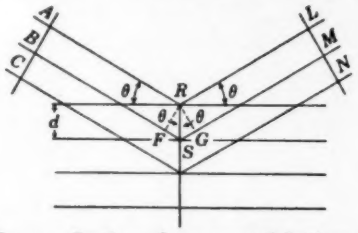



**Fig. 19. X-ray reflections from crystal lattice. The X-ray wave length (A to B) must have a dimension in the same order of magnitude as the lattice distance (d).**
From *Physical Chemistry*, F. Daniels and R. A. Alberty, John Wiley & Sons, Inc., (1955).

### 7.5 Summary

Fundamentally, if you wish to see particles, or particle effects, you use electromagnetic wave lengths which are in the neighborhood of dimension near that of the particle you wish to see. We are, of course, referring to limits on the small side and not to large dimensions.

The resolution (seeing detail or separating two particles) of the eye is normally near .02 cm. or 2,000,000 Å. The eye can determine the presence of a single particle by direct vision if its diameter is in the range of 100,000 Å. When oblique lighting is used, the location of somewhat smaller (perhaps 1/10) particles can be seen as a spot of light. Whiteness or turbidity may be evident because of the presence of many particles with sizes ranging from several hundred to several thousand Å—say 700 or 800 Å to 10,000 Å and over. (Actually there is no limit on the upper side when surfaces are irregular or rough.)

The sky or tobacco smoke or opal glasses may be bluish in color due to the presence of sufficient particles in the realm of a few Å (molecular) up to say 3000 Å.

All these dimensions must be considered as appropriate.

**Absence or Presence of Light-Scattering Particles and of Internal Surfaces**

As applied to transparency, the real concept is the intentional absence of such light-scattering particles if we wish to maintain transparency (Section 8.3). Or vice versa, if such particles are present, their surface effects must be made invisible (Section 9).

## 8. PARTICLES IN GASES, LIQUIDS AND SOLIDS (INCLUDING GLASSES)

We have set the stage for various effects of particles in relation to color and visibility. We cannot see an ordinary molecule of 3 to 5 Å in diameter. However, when we get a very thick layer of such molecules, and when perhaps some aggregates of molecules occur to give some increased size, we may get a transparent color effect. Such an effect is the blue of the sky or the red of the sunset (explained in Section 7.3).

### 8.1 Particles in Gases

(Reference 25) A similar effect is the blue color of cigarette smoke. Smoke which comes from industrial stacks is often black due to presence of carbon particles (unburned fuel). However, tobacco smoke is well filtered and has particles from about $1 \times 10^{-7}$ cm. up to $3 \times 10^{-5}$ cm. (or about 10 to 3000 Å). This smoke may have invisible particles in it, but still be colored blue due to the Rayleigh scattering effects (see Section 7.3). It also may have particles visible by light spots, and give a white light scattering.

Dust mixtures are somewhat larger in particle size. They may progress down to about $1 \times 10^{-4}$ cm. in size (10,000 Å). In this case they are white because of light spots and scattering. Similarly, dust particles may be much larger (up to .05 cm.). Really fine dust particles may be invisible by light scattering but still be responsible for health hazards. Fumes are in this realm of particle size (1000 to 10,000 Å).

Fog and rain are two extremes of particle size, as follows:

| | | |
|---|---|---|
| Fog, | .0005 to .005 cm. diameter (50,000 to 500,000Å) | |
| Mist, | .005 to .01 | cm. diameter |
| Drizzle, | .01 to .04 | " " |
| Rain, | .04 to .4 | " " |

Obviously, a slight rain in air can be quite transparent, but this transparency is due to large distances between rain drops. The analogy to transparency of gases, as already mentioned (Section 3), is plain. A heavy rain in air can be almost opaque, or at least one can see only a few feet distance. When we progress to a mist and a fog, we enter into the realm of light scattering.

When we grind up glass into particles, we get an opaque or white mass. The particles are mixed with air. Here both the air and the glass are individually transparent, but the mixture is white.

### 8.2 Particles in Liquids

Here we can have three cases: the presence of gas bubbles in liquids, solid particles in liquids, or liquid particles within liquids.

A mixture of salad oil (transparent) in water (transparent) can give an opaque or white emulsion when well dispersed by beating. This is an immiscible liquid emulsion. Neither liquid mixes with the other. There are samples of opaque glasses due to this same effect.

Gas bubbles in a liquid will give a white or opaque mixture, even though both are, separately, transparent.

A solid within a liquid gives light scattering. A case here is the presence of, say, limestone particles in a well of water. There are cases of bluish coloring in liquids due to chemical precipitates of very small particle sizes (for instance, silver particles within a photographic emulsion liquid).

### 8.3 Particles in Solids

(References 5, 11, 15) Once again we may have gases, solids, or liquids within solids and produce nontransparency due to an inhomogeneous mixture.

For gases within a glass, we cite two common illustrations. The porcelain enamel on your kitchen sink is nontransparent. Part of this is due to small gaseous bubles within the glass layer. (Also part is due to solid crystals within the glass.) This is not a common method of producing opaque glasses.

In opal glasses we have many gas bubbles. One study (Ref. 15) reports that their sizes vary between

$3 \times 10^{-6}$ cm. (300 Å)
and $8 \times 10^{-6}$ cm. (800 Å)

This size range is in the realm of Rayleigh scattering and the bluish color of opal glasses by transmitted light is partially due to these bubbles. The number of such bubbles is reported as from 1 to $10 \times 10^{9}$ per square centimeter of glass surface.

Opaque opal glasses also have crystals present. These are commonly calcium fluoride ($CaF_2$) in sizes from

$4 \times 10^{-6}$ cm. (400 Å)
to $3 \times 10^{-4}$ cm. (30,000 Å)

These are somewhat larger than the gas bubbles, and there are only about 1/10 as many crystals as bubbles present. These sizes cause both Rayleigh scattering and light scattering, but predominantly light scattering.

We have thus explained the bluish and whitish effects seen in opal glasses.

There are some colors of glass which are explained as being due to the presence of particles of colloidal dimension[1]. The most common such color is the gold ruby glass, in which the color is controlled carefully by control of the size of the gold particles. While the particles themselves are not visible (without magnification), they are present as gold in colloidal form and the color is due to the typical absorption of gold metal of this size. For instance, the desired particle size in a gold ruby glass is between 50 and 600 Å. (Ref. 5). When these dimensions are maintained, we have a good gold ruby color. When the particles grow, however, to the range of 700-1000 Å, we begin to get turbidity, and this turbidity is the result of light scattering. The color of the particles in general does not contribute to the color of the glass when you get into this range of size. When the particles are in the range from 2000 to 5000 Å, they contribute very little to the actual color and they definitely produce an intense scattering of light. Once again we must call attention to the fact that this scattering of light in this

[1]The colloidal state (Ref. 11) is now commonly recognized as a special state of matter containing particles within a certain dimension. The ranges usually covered are from $1 \times 10^{-7}$ to $5 \times 10^{-5}$ cm. (10 to 5000Å). (In considering the true colloidal state the particle must have all three dimensions within these limits. This is done in order to eliminate fine fibers and very fine films from the colloidal definition.) This size of particle falls between that normally considered atomic (1 to 10 Å) and that field just visible by the best known ordinary microscope (4000 Å).

Due to the fact that many crystals are in the range from 10 to 20 Å in some dimensions and that many large molecule materials, such as high polymers, etc., reach up to several hundred Å, it is obvious that the colloidal state overlaps definitely with crystal dimensions.

realm of 2000 to 5000 Å particle size is in the same realm as 4000 Å for wave length of blue light.

### 8.4 Summary

We have seen why some mixtures are opaque, white, colored, etc., from the viewpoint of size of particle present. These are explanations based on inhomogeneity, or index of refraction change, etc., which produce effects other than transparency.

**Homogeneity**

An index of refraction change at a surface causes bending, reflection, or refraction of light. The presence of the surfaces is really the presence of an inhomogeneity of large enough nature to have effect on light waves. Normally, surfaces of dimensions of 1/4 of the wave length of light used will give a noticeable inhomogeneity. This will give light scattering and visibility by scattering. The result is opacity, or loss of some transparency. When the particle size is still smaller, we get color effects. Both of these effects can occur in glass. Normal sized ground-up solids, including ground-up crystals, exhibit nontransparency due to particle surface.

## APPENDIX

Appendix 3

A unique and modern usage of transparency and optical properties of glass—the Owens-Illinois functional glass blocks (patents applied for):

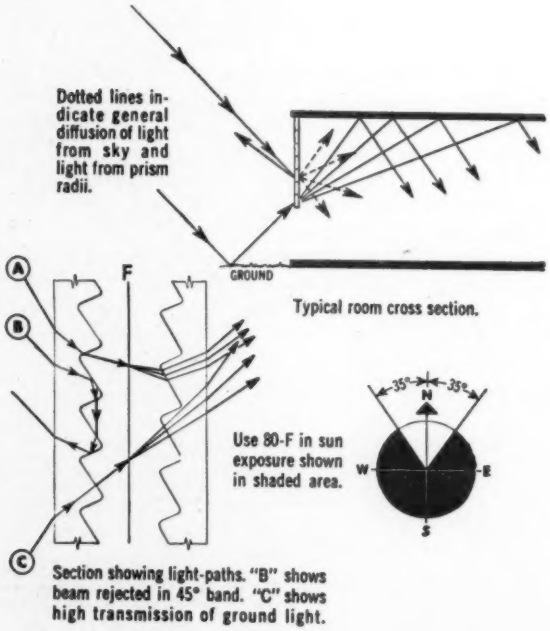
A new glass block design based on the principle of rejecting sunlight at the time when its intensity reaches a maximum on the exterior. Rejecting the peak intensity of solar energy reduces brightness problems to a minimum, and correspondingly reduces solar input. Distribution and diffusion of the daylight is excellent.

A. Light from high sun altitudes is transmitted efficiently by this block.

B. Light from a region of the sky approximately 45° above the horizontal is rejected. Note that rejection is by reflection, not absorption. The rejected light does not enter the cavity of the block. Light from the low sun angles and the lower sky is transmitted in increasing degree below 45° band.

C. Cool ground reflected light is transmitted with maximum efficiency.

References mentioned in this section are listed in the February issue of THE GLASS INDUSTRY, pages 112 and 114.




## F. J. SOLON OF O-I, ELECTED V.P. OF FREEDOM SHRINE FOUNDATION

Faustin J. Solon, vice president of Owens-Illinois Glass Company, has been elected vice president of the National Freedom Shrine Foundation and will move to Washington, D. C., to assume his new position.

Mr. Solon, long active in civic affairs and fund raising for charities and other activities, will continue his 47-year career with Owens-Illinois, although on a curtailed basis. In the new post, he will be responsible for raising funds for a Freedom Shrine to be built near the Washington Monument.

## C. M. BROWN, PITTSBURGH PLATE, DIES

Clarence M. Brown, 89, honorary chairman and a member of the board of directors of Pittsburgh Plate Glass Company, died February 9 at his home in Philadelphia.

Possessor of one of the longest records of active service to a corporation in the industrial history of the United States, Mr. Brown has been associated with Pittsburgh Plate Glass Company for more than 63 years. He has served as a director of the corporation since 1905.

He joined the company in 1895 as legal advisor to John Pitcairn, founder of the enterprise. Elected a director in 1905, he was named general counsel two years later and in 1922 became a vice president.

Mr. Brown was named chairman of the board during 1931 and served in that capacity for more than 25 years. Following his retirement as chairman in 1955, he was named honorary chairman and continued to serve as a director.

A native of New York City, Mr. Brown was educated at Temple University and was a graduate of the Law School of the University of Pennsylvania.

Following services at St. Paul's Episcopal Church, Chestnut Hill, private burial services were held at West Laurel Hill Cemetery.

Surviving are two daughters, Mrs. Lorna B. Haley of Plainfield, N.J. and Mrs. William G. Guernsey of Wellesley, Mass.; two sons, Howard B., and Robert M. Brown, both of Philadelphia, 11 grandchildren and two great grandchildren.

Mr. Brown was a director of the following companies: The Pitchairn Company, Insurance Company of North America, and Central Penn National Bank, Philadelphia.

# Spectra of Simple Glasses in the Infrared Range and their Relations to the Structure of Glass

By V. A. FLORINSKAYA and R. S. PECHENKINA
Free Translation of the Russian Original Text
By WILHELM EITEL, Institute of Silicate Research
University of Toledo, Toledo, Ohio

PART III

## THE STRUCTURE OF SODIUM SILICATE GLASSES

THE STUDY OF THE SPECTRA of sodium silicate glasses as a function of their composition and thermal processing convinces us of the fact that the atomic distribution in the glass is not entirely at random. In the formation of the structure of soda glasses, silica and many silicates participate. These correspond to definite chemical compounds, and types of crystalline solutions. It is not easy, however, to discriminate between them in particular.

The process of glass formation of the sodium silicate type is apparently somewhat different from that of the lead glasses.

By comparing the transmission spectra for films blown from a glass melt, with the transmission spectra of powders of the massive glass*, it becomes evident that certain elements in the spectra of the film and the glass (powder), are quite similar; others, however, are different (see Fig. 10, a, b). Evidently, there are in the glass melt certain atomic groups which are built up in a manner similar to those in the glass, whereas other groups of atoms exist which are stable only in the range of high temperatures (compare portions of the spectra near 9.6 $\mu$ and 10.8 $\mu$).

As in lead glass, evidently the sodium ions are not distributed entirely at random in the melt according to statistical laws, but enter well-defined atomic formations by interactions with the silicon and oxygen ions. In contrast with the lead ion, however, the sodium ion does not play the role of a central-bonded ion; instead, it forms groups which are stable at high temperatures, but become unstable at lower temperatures and thus are compelled to disintegrate and become rearranged in other groups.

Because the cooling process goes on relatively abruptly, only a part of the groups have enough time to rearrange and the residual groups are "frozen-in". Therefore, a glass contains, side by side, such structural formations which are preserved from the state representing the melt to the state that is stable at room temperature, and likewise quite a series of transitional structures. Thus may be explained, perhaps, the strong distinction in certain properties of lead and sodium glasses. According to the data of Kuznetsov and Mel'nikova [15], e.g. the electrical conductance of lead glasses is a million times lower than the electrical conductance of sodium glasses. According to the results of Evstrop'ev and Skornyakov [16] the difference of the energy contents between the glass and of the silicate is considerably smaller for the lead silicate system than for the corresponding difference in the sodium silicate system.

In the structure of a glass cooled down to room temperature there are groups with a regular distribution of the atoms which are similar to the distribution in the silicates which are segregated during the crystallization of the glass. As an example, we consider the spectra of the binary glass with 33.3 molec. per cent $Na_2O$ and 66.7 molec. per cent $SiO_2$. This glass was selected because its structure was investigated by many methods. There are studies by X-ray methods of Russian physicists who recognized the existence of a defined chemical compound (sodium metasilicate) and of crystallites in the glass. [13] [14]. It is generally known that American investigators negated by their results of X-ray analysis the possibility of the existence, with any regularity [17], of defined chemical compounds in a glass.

There is a series of investigations by the coworkers in the laboratory of I. V. Grebenshchikov, in which the behavior of some physical and chemical properties of sodium silicate glasses were studied. Based on their results, these authors concluded that one defined chemical compound, namely sodium disilicate, existed in the glass [16].

In the laboratory of Vuks and Ioffe [18] the spectra of the combination (Raman) scattering of the same glasses were investigated; the authors came to the conclusion that the disilicate is present in a glass with 33.3 per cent $Na_2O$. Finally, a publication of Gross and Kolesova [19] was presented on the same meeting in which the existence of the sodium disilicate in this glass was negated.

In the curve (a) of Fig. 11 is shown the functional relation of the reflection coefficient in the range from 8 to 11 $\mu$ with the wave-lengths (the first fundamental band of selective reflection).* Assuming that the $[SiO_4]$ tetrahedra are distributed entirely at random in the glass, then quite an assembly of frequencies, distributed around a certain average position which corresponds to the most probable frequency, must exist for one and the same type of oscillations of the tetrahedron. The reflection curve must in this case be totally diffuse. An analogous curve may be observed also in this case if there is simultaneously a series of atomic groups with different structures (among which regular ones may also occur) which

*Layers of the powders were prepared by special methods which were developed for the investigation of the spectra of unstable substances.

*In the reflection spectrum of glasses having the composition of sodium disilicate occasionally a band was found at 10.5 to 10.6 $\mu$, while in other cases it was absent. The nature of this band remains for the present not entirely clear. Evidently, it is determined by the same factors which control the band at 10.8 $\mu$ in Fig. 10, a.

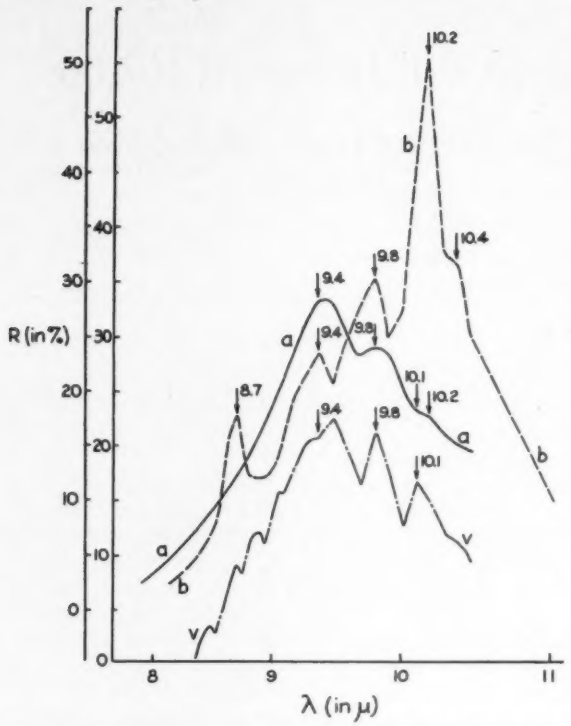



**Fig. 11. Reflection spectra for the glass of sodium disilicate composition in the range from 8 to 10.5 μ after different thermal processing.**
**a- the initial glass; b- crystallized at 620°; v- glass in the state before the crystallization.**

give bands situated near to, but partially overlapping, one another. In the case discussed here, however, the band has a distinct structure which indicates the differentiation of the bondings. There are reflection maxima at 9.4 and 9.8 μ and a weak flexure in the range from 10.1 to 10.2 μ.

In the spectrum of the powder the fundamental transmission minimum lies at 9.4 μ, and in the fine-structure a series of weak minima is also observed among which there are those of the wave lengths 9.8 and 10.1 to 10.2 μ. The spectrum of a film, compared to that of the powder, is rich in minima in the range from 10.1 to 10.4 μ which overlap and give a band with a minimum at 9.4 μ, and a second band and in the range from 10.1 to 10.4 μ.

It may be said that the association of such structural formations gives a first fundamental band of reflection of the type seen in Fig. 11a. These spectra may be deciphered by a study of the progressive crystallization, and a systematic observation of the way the spectra behave. After the glass was crystallized by heating for 48 hours at 620° the curve a was changed to the curve b. The first maximum at 9.4 μ became sharper, but weaker, in its intensity. The second maximum at 9.8 μ became sharper and degenerated. At 10.2 μ, where only a weak terrace previously occurred, now arose the strongest reflection maximum, and new maxima appeared at 8.7 and 10.4 μ.

To decipher the course of curve b for a glass of exactly the same melt, another series of melts was crystallized at different temperatures and their reflection and transmission spectra compared. It was found that in the crystallization of this glass, silica was segregated together with some silicates. Sodium disilicate appeared in its two modifications α and β (the inversion temperature of which is about 680°) as the principal crystallization product. If the glass crystallized at 620°, i.e. below the inversion temperature $\alpha \rightleftharpoons \beta$, both modifications were segregated at the same time. But at a subsequent exposure of the crystallized glass, at constant temperature, the α-modification was converted to the β-modification. If the glass was crystallized at 700° the α-form is apparently the principal product and the β-modification is accessory, despite the fact that both modifications are segregated. Their spectra are sharply distinct.

In Fig. 12 is shown by curve (a) the transmission of a layer of the powder of the crystallized glass in the range of the fundamental absorption band when the β-modification is the principal phase. The minimum transmission is at 10.2 μ, with traces of a second minimum at 9.8 μ. In the range of the second fundamental absorption band the transmission minimum of the layer lies at 13.2 μ (curve a'). In curve b is represented the analogous transmission spectrum when the α-modification is the principal product of crystallization. The main transmission minimum lies at 9.8 μ. The band at 13 μ (curve b') is by far sharper than the analogous band of the β-modification, and has a transmission minimum at 13.0 μ.

The principal absorption maxima (i.e. transmission minima) of the first band for one and the same type of oscillation of the atoms in the $[SiO_4]$ tetrahedra diverge by .0.40 to 0.45 μ. This is a very great spectroscopic distance! The spectra of lattices of silicates of even dif-

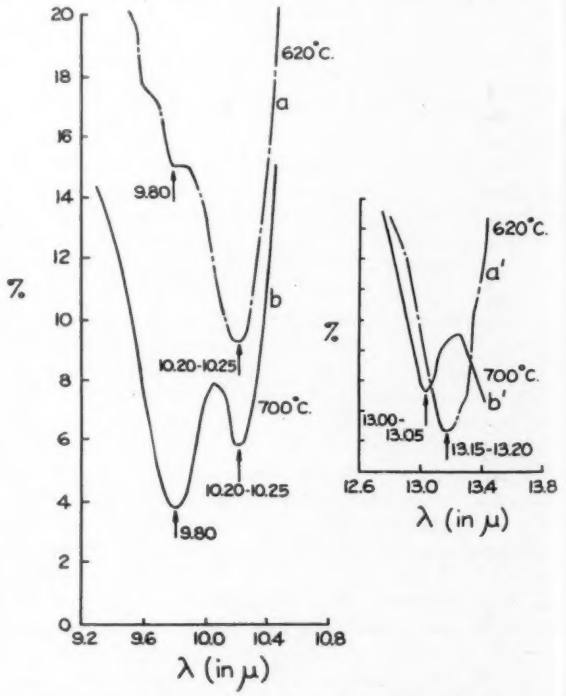



**Fig. 12. Transmission spectra of thin layers of the powders of sodium disilicate glass, crystallized at 620° (curves a and a'), and 700° (b and b'), in the range of the first and second fundamental absorption band.**

ferent classes may differ by such a considerable amount. If one compares the spectra observed with the reflection data of silicates with different structures (1) one may, by the position of the principal reflection maximum in the first fundamental band of the spectrum, immediately refer the $\beta$-modification of sodium disilicate to the class of chain silicates. The spectrum of the $\alpha$-modification belongs, however to the class of spectra with layer structures.

The investigation of the crystallization products by crystallooptical methods which was kindly performed by E. Ya. Mukhin, demonstrated that the crystals of the $\alpha$-modification have a tabular habit, whereas those of the $\beta$-modification are developed into bundles of aggregated fibers or needles. The indices of refraction in the visible range are very similar for the acicular and the tabular forms. During the crystallization of the glass with 33.3 per cent $Na_2O$ at 620° nearly always both modifications of the disilicate were segregated in our experiments, but by a subsequent heat exposure the $\alpha$-modification was inverted to the $\beta$-form. There were some cases (always rare) in which nearly only the $\alpha$-modification was segregated.

In Fig. 13 the transmission spectra for powders of glasses crystallized at 620° are shown. The curves a, b, v belong to exposure time periods of 1 hour, 2, and 12 hours, respectively. First, the $\alpha$-modification is segregated (a minimum of the transmission curve lies at 9.8 $\mu$), with a slight admixture of the $\beta$-modification. Then, it is purified from some intermediate structure which it replaces. Two other intermediate structures replacing this transitional structure finally are reorganized to the $\beta$-form. The last of the curves shows that after 12 hours the $\beta$-modification prevails.

When the glass is crystallized at temperatures between 710° and 720° the bands of the $\beta$-modification appear in the transmission spectrum besides the bands belonging to the $\alpha$-modification (which prevails as in the case of the crystallization at 700°). Some weak bands were also observed which we could refer only to some unknown silicates which are stable above 710°.

Let us now return to the reflection spectrum of the crystallized glass. From the data given above it is concluded that the maxima at 9.8 and 10.2 $\mu$ belong to the $\alpha$- and $\beta$-modifications of sodium disilicate, respectively. Therefore, analogous diffuse maxima in the initial glass also correspond to formations which have an atomic position similar to that in sodium disilicate, i.e. to sodium disilicate crystallites. Of all the sodium silicates which we have investigated, only the $\alpha$-disilicate has a band at 9.8 $\mu$.

What is happening in a glass of a structure with the maximum at 9.4 $\mu$? Crystals showing the first fundamental reflection band at 9.4$\mu$ are partially segregated during the crystallization of a glass of sodium disilicate composition. Evidently, one must assume that they are crystalline solutions. With reference to the structural formations in the glass which give the maximum at 9.4 $\mu$ on the reflection curve, one can say at the present time only that the degree of tetrahedral association in these must be much stronger than in sodium disilicate. In comparison to the remaining structure one must assume that it is richer in silica, i.e. has a somewhat different composition. During crystallization, free silica is first formed, as is indicated by the appearance of weak maxima in the range of 8.5 to 9.0 $\mu$ on curve v in Fig. 11 which represents the reflection coefficient of the same glass in the state of starting crystallization.

The Liquidus temperature of the glass here considered lies at 876°. The sample was heated some degrees higher

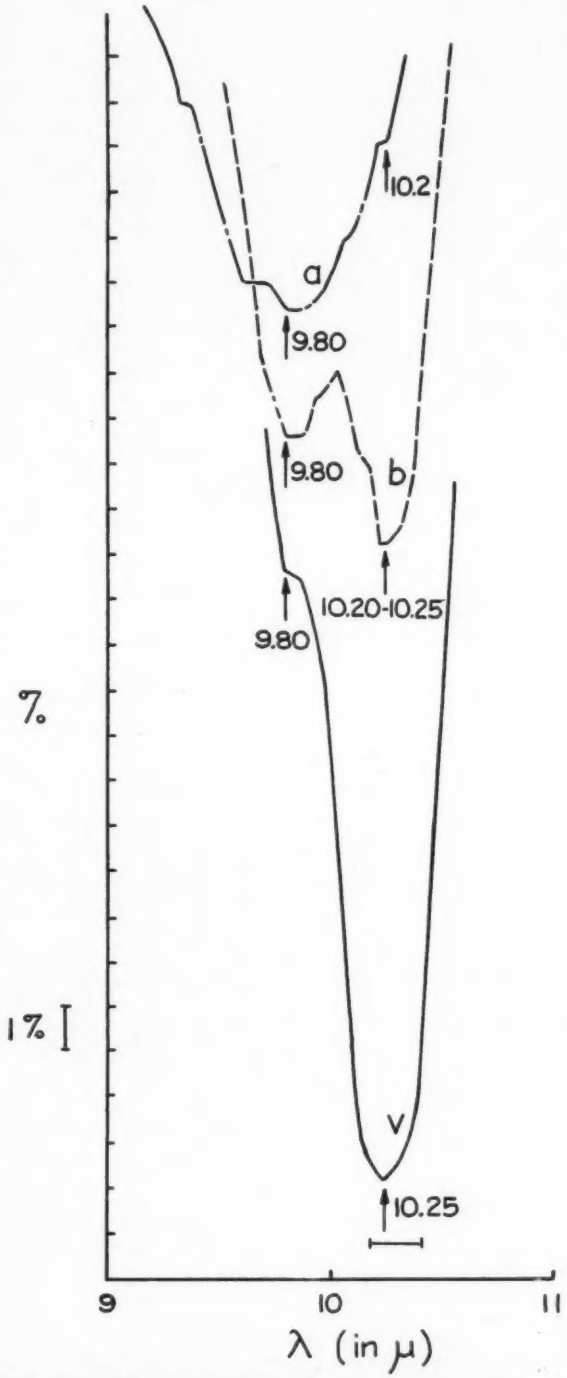



**Fig. 13. Changes in the transmission spectra of a layer of powder in the transition of the $\alpha$-modification of sodium disilicate (a) into the $\beta$-modification (b).**

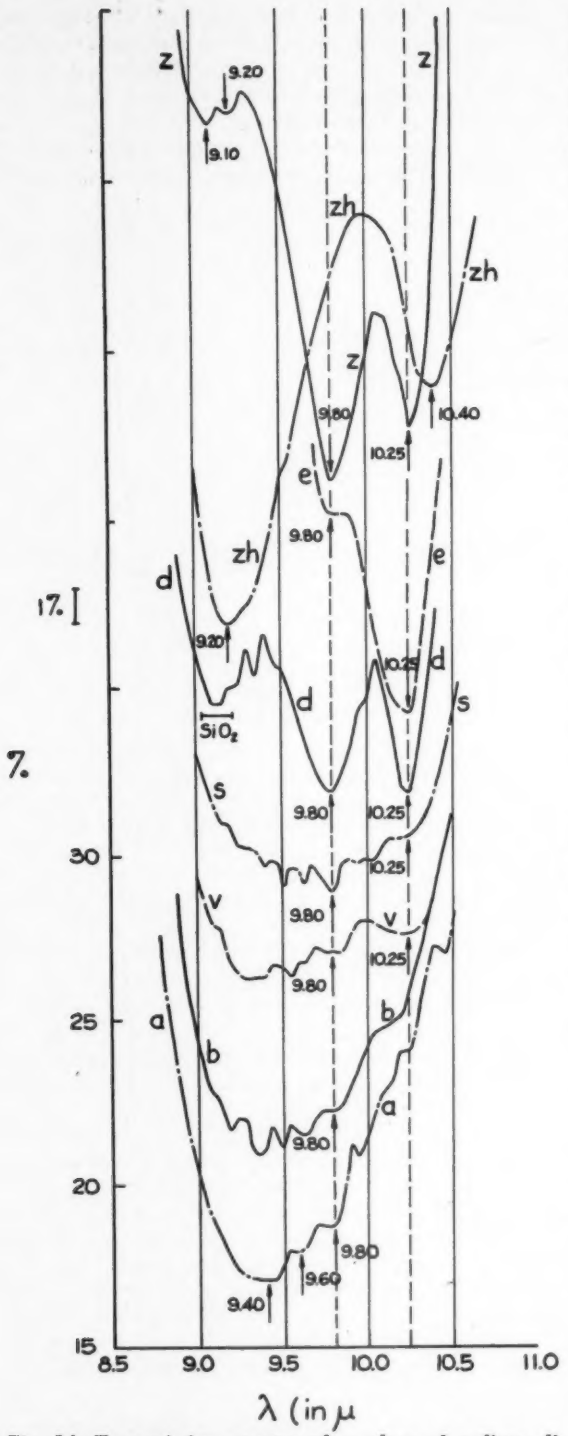



**Fig. 14. Transmission spectra of a glass of sodium disilicate composition in the range from 9 to 10.5 μ after different thermal treatments.**

**a- a thin layer of the powder of the initial glass; b- same, of a glass heat-exposed at 620° for 3 hours; v- the same, for 6 hours; g- the same, for 3 hours; d- the same, for 12 hours (exterior entirely crystallized portion of the glass, crust); e- the same, heated at 620° for 48 hours; zh- the same, for 12 hours (inner not crystallized portion of the glass, core); z- the same, from the core, entirely crystallized at 620° which previously showed the spectrum zh.**

than 876° and was kept in the molten state for 10 days enabling the liquid to come into substantial equilibrium in this period. After that, the glass was sharply cooled in order to impede segregation of a primary phase at the Liquidus point. The glass was ready to crystallize, but it was not able to do so and remained without any indications of turbidity. As seen from curve v, the spectrum is sharply detailed; the segregation of the α-modification of sodium disilicate was strongly indicated by the band at 9.8 μ and one of those silicates stable above 710° was indicated by the band at 10.1 μ. This is the fourth silicate in our enumeration which participates in the development of the structure of this glass.

What happened now concerning the structure with the maximum at 9.4 μ? A portion of it was rearranged into a structure which is next to the α-modification. But during this rearrangement a certain portion of free silica was evolved which is indicated by the weak maxima in the wave length range of the maxima of selective reflection for silica (8.4 to 9.0 μ).

Let us now consider how the crystallization process occurs at low temperatures. Because we used a really ultra-pure glass the crystallization occurred very abruptly. For instance, samples of some melts crystallized completely at 620° in 1/4 to 1 hour while in some others the crystallization set in only after 12 hours. We used one of the latter samples for the observation of the behavior of the glass as a function of time at this temperature.

From Fig. 14 the curves a to zh represent the transmission spectra of powders of the initial glass and after heating for 3, 6, 8, and 12 hours. Until 11 hours of heating, the glass did not show any traces of turbidity. By observing the greatest caution in taking the samples, the exterior portion of the pieces was removed. After 12 hours of heating the glass crystallized very well in the exterior parts as in the whole mass but only the innermost portion of the sample remained vitreous and without showing any traces of turbidity. We took the transmission spectra of the crust (curve d) and of the central core (curve zh) separately.

According to the data of G. O. Bagdyk'yants, who undertook simultaneously with us, a systematic investigation by electron diffraction methods of the same objects, the glasses a, b, v, and zh showed only diffuse rings in the electron diagrams. The glass heated for 8 hours was not studied by him.

The transmission curve of the initial glass has a minimum at 9.4 μ. After 3 hours of heating this minimum became decreased and split up. All the curves were much flattened. The association of pure silica started. After 6 hours of heating the minimum at 9.8 μ which corresponds to the α-modification was well developed and, also the minimum at 10.2 μ, which belongs to the β-modification. After 8 hours of heating the minimum at 9.4 μ disappeared and the minimum at 9.8 μ became predominant. A prolonged heat exposure brought about the segregation of the two forms of the disilicate (9.80 and 10.20 to 10.25 μ), and silica (9.15 μ). The examination by crystal-optical methods of the crystallization products also demonstrated that silica together with the two modifications of sodium disilicate was segregated. A further heat expo-

(*Continued on page* 168)

# Structural Interpretation of Immiscibility in Oxide Systems

• PREVIOUSLY UNRELATED DATA on immiscibility in oxide systems have been interpreted structurally under a unified theory. [1] Ernest M. Levin and Stanley Block of the National Bureau of Standards' mineral products laboratories have applied crystal chemistry principles to the quantitative interpretation of immiscibility in 19 binary and 24 ternary oxide systems.

Liquid immiscibility is frequently observed in binary and ternary oxide mixtures composed of glass formers, such as silicon dioxide and boric oxide, and glass modifiers, such as barium oxide and magnesium oxide. From a practical standpoint the understanding of the phenomenon of liquid immiscibility in oxide systems is important because of its possible effects in the production of industrial products, such as glasses, slags, and cements. From a theoretical standpoint the study of immiscibility offers another approach to the explanation of the structure of oxide melts.

The fundamental equation for immiscibility in a binary system is: $X = 100M/0.602ds^3$, where X is the weight percent of the modifier; M its molecular weight; d the density; and s the average cation separation. This equation shows that if the density and average cation separation in the modifier-rich liquid are known exactly, its composition can be accurately determined. Alternatively, if the composition and density of the modifier-rich liquid are known, the cation separation may be calculated. The latter procedure was employed to calculate cation separations in known borate and silicate systems. The resulting values were compared with separations calculated from previously suggested coordination configurations. [2] The appropriate coordination could then be determined.

A simple configuration—two cations bonded to the same oxygen atom—was found to occur with divalent cations having ionic radii less than that of $Ca^{++}$, for example $Cd^{++}$, $Zn^{++}$, and $MG^{++}$. In this case the ionic separation for a 180° bond angle is twice the sum of the ionic radii of oxygen and the modifier cation. Cations of ionic radii greater than of $Ca^{++}$—for example, $Sr^{++}$, $Pb^{++}$, and $Ba^{++}$—are bonded to opposite pairs of oxygen atoms of a tetrahedron. In calculations for this type of ionic separation, the known tetrahedral distances for $SiO_2$ and $B_2O_3$ were used. Calcium was found to occupy a transition position, being mainly in the simpler configuration in the silicate system and in the more intricate configuration in the borate system.

From the cation separation and an approximation for the density, the composition of a modifier-rich liquid can be obtained. To provide another check on the postulated coordination configuration, a second method of calculating immiscibility was developed. The method involves ionic radii, appropriate coordination type, and the volume of space occupied by an oxygen atom. The volume of melt containing one cation is given by the cube of the cation separation. The cation separation is calculated from geometrical considerations of the appropriate coordination type as mentioned above. A correction can be estimated for the volume of space occupied by the modifier cation. The remaining volume is occupied by oxygen atoms, in close packed arrangement, and glass-forming cations, which are located in the interstices and consequently do not occupy additional space. From the adjusted volume of oxygen atoms per cation, the number of oxygens per cation can be estimated. From the number of oxygens, the nominal oxide formula for the modifier-rich liquid is computed. Calculations by the two methods give values for composition which agree within the limits of experimental error with most of the recorded data.

Immiscibility in ternary systems can be calculated by application and extension of these same principles. Three types of ternary systems have been considered. The first and simplest type consists of two modifier oxides and a glass former. In these cases the two liquid-one liquid boundary as plotted in a phase diagram is essentially a straight line indicating that immiscibility within the ternary system is an additive function of the two binary immiscibilities.

A second type of immiscibility boundary occurs in systems containing two glass formers and one modifier oxide. In this case the maximum amount of modifier in the immiscible liquids occurs within the ternary system. Immiscibility varies inversely as the cube of the cation separation. Therefore a small decrease in cation separation can cause a relatively large increase in immiscibility. A decrease in separation is possible when modifiers in the more involved configuration change to the simpler type or when the usual bond angle found in the simpler type is reduced, as when a cation changes from octahedral to tetrahedral coordination. Calculation based on such premises give good agreement with observed data.

A third type of immiscibility occurs in systems containing an alkali or alumina, a glass former, and a modifier oxide. In such systems immiscibility is confined to a narrow region along the modifier-glass former boundry. Therefore the addition of a small amount of alumina or alkali to a binary system with immiscibility gives complete liquid miscibility. The alumina or alkali acts as a homogenizer to coordinate incompatible structural units of the melt. From postulated configurations consistent with previous deductions, two methods are derived which yield a quantitative estimate of the amount of homogenizer required for complete mixing in ternary borate and silicate systems.

Observed phenomena were interpreted on the theory of electrostatic bond strength in conjunction with charge distribution. The analysis of immiscibility has led to numerous implications bearing on the structure of glass.

A noteworthy conclusion is that the modifier-rich melt may be considered to be composed of a pseudo-unit cell, the size of which is determined by the cation separation.

**Table 1. Comparison of National Bureau of Standards Calculated Compositions of Modifier-Rich Liquids in Borate Systems with Observed Data.**

| | | Calculated by: | |
|---|---|---|---|
| Modifier | Experimental | Density | Oxygen Volume |
| | mol. per cent | mol. per cent | mol. per cent |
| BaO | 16 | 18 | 16 |
| PbO | 19 | 21 | 18 |
| SrO | 21 | 21 | 20 |
| CaO (a) | 27 | 23 | 22 |
| CdO | 39 | 38 | 38 |
| ZnO | 48 | 49 | 46 |
| CoO | — | 42 | 47 |
| MgO | 49 | 52 | 50 |

(a) Calcium represents the transition cation between the two types of coordination found for cations of radii less than and greater than calcium.

(1) Structural interpretation of immiscibility in oxide systems, by Ernest M. Levin and Stanley Block. Part I. Analysis and calculation of immiscibility. *J. Am. Ceram. Soc.*, *40*, 95 (March 1957). Part II. Coordination principles applied to immiscibility, *J. Am. Ceram. Soc.*, *40*, 113 (April 1957). Part III. Effect of Alkalies and alumina in ternary systems, *J. Am. Ceram. Soc.* (on press).
(2) Atomic consideration of immiscibility in glass systems, by B. E. Warren and A. G. Pincus, *J. Am. Ceram. Soc.*, *23*, 301 (October 1940).

## M. A. EDDY, OF E. R. SQUIBB, DIES

Maxson A. Eddy of 60 Sutton Place South, New York City, died February 13 of a heart attack. His age was 54.

At the time of his death, Mr. Eddy was director of packaging for the pharmaceutical firm of E. R. Squibb & Sons, division of Olin Mathieson Chemical Corporation.

A graduate of the University of Connecticut with a Bachelor of Science degree in chemistry, class of 1925, Mr. Eddy launched his business career as a ceramic engineer for the Hartford Empire Company, Hartford, Conn. In 1932 he joined Owens-Illinois Glass Company as eastern director for research and development. He was plant manager of Owens' Terre Haute, Indiana manufacturing facility when he left the firm in 1938 to become manager of operations of the Kimball Glass Company, Vineland, N.J. Owens-Illinois Glass Co. purchased the Kimball firm in 1947 and Mr. Eddy was named general manufacturing manager for the Kimball Glass Division.

In January, 1949, Eddy accepted a position as general manager of the Wheaton Glass Co., Millville, New Jersey. He ended his association with this firm and formed his own concern, the Eddy Glass Co., in Ocean City, N. J. Mr. Eddy headed this enterprise through January, 1955, at which point he joined E. R. Squibb & Sons. A member of the Drug and Chemical Club of New York as well as the Drug, Chemical and Allied Trade Section of the New York Board of Trade, Inc., Mr. Eddy was also an associate member of the Packaging Institute.

## AMERICAN POTASH PROMOTES F. MARSIC AND H. DeARMOND

Frederick Marsic has been elected secretary of American Potash & Chemical Corporation and Henry DeArmond assistant secretary, according to an announcement by Peter Colefax, president. The officers were named following the election of Richard J. Hefler, formerly company secretary and assistant to the president, as vice president in charge of finance.

F. Marsic

H. DeArmond

Marsic, formerly assistant secretary, retains his other positions as assistant treasurer and office manager at company headquarters at Los Angeles. DeArmond was administrative assistant prior to his present appointment.

Marsic is the longest service employee of American Potash, having been with the company nearly 45 years. He joined the company in 1913 as an office boy at AP&CC headquarters, then in New York. After being promoted to chief accountant, he was named assistant secretary and assistant treasurer in 1942. In 1946, when the company moved headquarters to Los Angeles, Marsic was transferred to California and was named office manager of the main office.

## R. E. GROETHE JOINS JESSOP STEEL

Jessop Steel Company has recently announced the appointment of R. E. Groethe to the staff of the company's metallurgical department. Before coming to Jessop Steel, Mr. Groethe was manager of the metallurgical department for Corning Glass Works where he became familiar with many applications for steels used in the glass industry.

Mr. Groethe was a metallurgist at the steel and tube division of Timken Roller Bearing Company before going to Corning in 1948. While at Timken he worked in production metallurgy, handling tool, alloy and stainless steel, and gained experience in the company's forge shop. Mr. Groethe graduated in 1941 from the South Dakota School of Mines as a metallurgical engineer.

## P. S. DUNN IS DIRECTOR AT AP&CC

Parker S. Dunn, vice president, manufacturing, of American Potash & Chemical Corporation, has been elected to the company's board of directors, according to an announcement by Peter Colefax, president.

At the same time, the board was increased from eight to nine members.

Mr. Dunn joined AP&CC in 1951.

# Inventions and Inventors

## Annealing and Tempering

*Annealing Glass. Patent No. 2,774,190.* Filed May 18, 1953. Issued Dec. 18, 1956. Five sheets of drawings; none reproduced. Assigned to Pittsburgh Plate Glass Company by Florian V. Atkeson.

This invention relates in general to the annealing of glass and more specifically to a method of substantially uniform control of the temperature of the cooling glass as it passes through the annealing range in order to obtain the glass characteristics desired.

It has been found that the residual stress present in annealed glass is a function of the time the glass is kept within its annealing temperature range and the manner in which the glass is cooled through said range. There is an optimum range of residual stress in glass which renders the glass most suitable for cutting. High stress values tend to increase cutting difficulties by increasing the tendency of a running fracture to depart from a score line made by a cutting tool. Stress values which are too low indicate the glass is too well annealed; the latter is said to be dead and difficult to cut.

The invention provides an annealing section for use in the manufacture of glass wherein the rate of cooling of the glass is controlled: the glass is cooled very rapidly from its molten state to a temperature substantially at the upper limit or top of the annealing temperature range, held at the top of the range for a short time, then cooled slowly but at an increasing rate through the range, and then cooled comparatively rapidly below the range, to produce annealed glass having a desirable, residual stress pattern.

There were 6 claims and 12 references cited in this patent.

## Feeding and Forming

*Apparatus for Forming Mineral Fibers. Patent No. 2,775,850.* Filed March 2, 1953. Issued Jan. 1, 1957. Two sheets of drawings; none reproduced. Assigned to Owens-Corning Fiberglas Corporation by Charles J. Stalego.

An improved fiber forming element is shown. The element comprises a precious metal bottom plate for a glass melter. The plate has ridges that are integral with the plate and protrude below the body of the plate. The ridges are parallel and spaced laterally with each other. Each ridge has an upward divergent side wall and a plurality of longitudinally spaced, downward directed orifices. The diverging side walls and ridges tend to dissipate heat sufficiently and rapidly enough to prevent flooding between orifices. The inhibiting of lateral flooding is highly important to continued operation of the fiber forming operation.

One claim and the following references were cited in this patent: 2,407,295, Simison et al., Sept. 10, 1946; 2,460,547, Stevens, Feb. 1, 1949; 2,489,508, Stalego, Nov. 29, 1949; 2,578,986, Schoonenberg et al., Dec. 18, 1951; and 2,634,553, Russell, Apr. 14, 1953.

## Furnaces

*Glass Melting Furnace. Patent No. 2,780,890.* Filed June 12, 1952. Issued February 12, 1957. Seven sheets of drawings; none reproduced. Assigned to Owens-Corning Fiberglas Corporation by Robert G. Russell.

This invention relates to glass melting furnaces and more particularly to a furnace designed for a continuous melting operation, for example, the continuous production of glass filaments or fibers.

A furnace structure is shown by means of which molten glass is moved through a tortuous path over heating surfaces which continuously apply heat to the flowing mass so as to present the molten glass to several orifices at the same or substantially the same temperature. Mechanical means are also provided for agitating the glass during its flow for homogenizing and dispersing impurities. Also provided are means for maintaining pressure and controlled flow characteristics within the mass of glass. The feeding of the glass out of the bushing under pressure is a particular advantage from the standpoint of control of fiber size and rate of production, that is, yardage per hour or weight per hour.

There were 15 claims and 13 references cited in this patent.

*Apparatus for Melting Glass. Patent No. 2,780,891.* Filed May 11, 1951. Issued February 12, 1957. One sheet of drawings; none reproduced. Assigned to Societe Anonyme des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, Chauny & Cirey by Pierre Arbeit.

This invention has for its object the provision of material obstacles made of graphite capable of retaining in the melting zone the glass making materials floating on the molten glass, while still permitting the circulation of the molten glass at the surface, as well as beneath the mass of raw materials.

The mass of glass making materials is retained in the melting zone by disposing therein discontinuous graphitic material obstacles rising at least to the level of the base of the mass of materials floating on the molten glass. It is also possible to use the material obstacles continuously over the entire width of the furnace, situated below the upper level of the glass bath and having a reduced height for enabling the circulation of the molten glass below and above said obstacle.

The mass of composition charged into the furnace constitutes a floating body, which is rapidly rendered relatively compact by the commencement of the fusion of its own materials, and which sinks to a greater extent into the molten glass the more intense the load per unit area of the surface covered thereby. The submerged portion of this mass comes into contact with the obstacles and the latter,, even when spaced apart, suffice to retain the whole of the mass which has not yet been fused. On the other hand, the current of molten glass is freely established beneath the obstacles, or between the latter in order to traverse the length of the furnace, be sub-

jected to the appropriate treatments and arrive at the point of utilization.

The technique is said to improve the efficiency of the furnace, reduce the quantity of heat used and permit the use of smaller furnaces.

There were 6 claims and 15 references cited in this patent.

## Glass Compositions

*Glass Composition. Patent No. 2,774,675.* Filed February 25, 1953. Issued Dec. 18, 1956. No sheets of drawings. Assigned to Owens-Corning Fiberglas Corporation by Games Slayter.

This invention relates to a glass composition and particularly to such a composition comprising a multiphase system, including one or more components having a high modulus of elasticity and one or more components having a relatively low modulus of elasticity. It relates more particularly to such compositions in massive or fibrous form having exceptionally high strengths and resistance to propagation of cracks.

It is apparent that glass compositions having from 40 to 50 parts by weight of a network former such as alumina and from 35 to 50 parts by weight of a flux or modifier such as calcia along with from 5 to 20 parts by weight of a stabilizing oxide such as tin oxide are suitable for the purpose of this invention.

It has been discovered that such glass compositions have a Young's modulus of elasticity considerably greater than that of most glass compositions containing silica. The modulus of these compositions has been measured by the sonic method and found to be as high as 16,000,000 while the greater proportion of glass compositions have a modulus of elasticity of from 10,000,000 to 12,000,000.

The glasses are very hard, having a hardness on the Moh's scale of from 6 to 7 while most glasses have a hardness of from 5 to 6. As a result of this hardness, the glasses are very insensitive to scratches and have, in addition, very high abrasion resistance. In addition to these properties, it has been discovered that the resulting glass compositions tend to be resistant to propagation of cracks through the glass itself. It is believed that this results from a true two phase system which comprises the low modulus component calcia and the high modulus component alumina.

Another advantage of these glass compositions lies in the fact that the glass has a high oxygen content and as a result coloring agents are maintained in a high state of oxidation which results in very clear colors. These compositions are readily adaptable for use both in the massive state and in the fibrous state.

In place of the alumina, such network formers as titania or zirconia may be used.

There were 8 claims and the following references cited in this patent: 1,736,642, Beaudry, Nov. 19, 1929; 2,090,098, Berger et al., Aug. 17, 1937; 2,172,839, Francis et al., Sept. 12, 1939; 2,240,327, Elenbaas et al., Apr. 29, 1941; 2,252,495, Dusing, Aug. 12, 1941; 2,486,812, Weyl, Nov. 1, 1949; 165,052, Great Britain, 1921; and 495,654, Great Britain, 1938.

## Glass Wool and Fiber

*Composite Glass and Asbestos Yarn. Patent No. 2,778,763.* Filed January 18, 1954. Issued Jan. 22, 1957. One sheet of drawings; none reproduced. Assigned to Raybestos-Manhattan, Inc., by Izador J. Novak.

A method has been discovered of safely reducing or eliminating the harsh and destructive contact of glass fibers by interposing between the glass filaments a cushion or mat of the very fine diameter chrysotile asbestos fibers to produce smooth, uniform diameter yarn of improved physical properties.

The relative diameters of these two fibers are widely separated, allowing the fine chrysotile fibers to act as a matting between the much larger diameter glass fibers. Drawn glass fiber for yarn runs from about 1 micron to 10 mircons in diameter, while naturally occurring chrysotile fiber in unitary form is from about .02 to about .05 microns in diameter. Hence the latter is well adapted to form a protective mat or cushion for the former, when first adequately separated into single fibers and then applied to the glass fiber.

There were 2 claims and the following references cited in this patent: 2,215,150, Hannen, Sept. 17, 1940; 2,230,271, Simpson, Feb. 4, 1941; 2,517,753, Ximinez et al, Aug. 8, 1950; 2,626,213, Novak, Jan. 30, 1953; 2,681,870, Novak, June 22, 1954; and 2,710,275, Waggoner, June 7, 1955.

*Coating Glass Filaments with Metal. Patent No. 2,772,518.* Filed November 10, 1952. Issued Dec. 4, 1956. Two sheets of drawings; none reproduced. Assigned to Owens-Corning Fiberglas Corp. by Harry B. Whitehurst.

It is well known that glass filaments have extremely high strength characteristics as well as highly desirable flexing characteristics which make them of particular advantage for many uses and applications as reinforcing agents. Such fibers, however, have a weakness to surface abrasion which reduces their ability to withstand wear, to the extent that it eliminates the possibility of their application for many uses in which the strength flexibility of the filaments would be highly desirable. The coating of glass filaments with metals, such as copper, zinc, aluminum, silver, or alloys therof, it has been found, is highly successful in providing protection against abrasion, but difficulty has been experienced in applying the metal to such filaments at a high rate of speed and with uniformity so as to make it economically feasible for mass production.

The present invention provides a new method and means for applying metal to glass filaments which permits economical production of coated filaments at a high rate of speed and at the same time providing coating uniformly which assures positive securement of the metal to the filaments and the desired degree of coating of the individual filaments by the metal along their length.

There were 10 claims and the following references cited in this patent: 1,934,796, Friederick, Nov. 14, 1933; 2,272,588, Simison, Feb. 10, 1942; 2,373,078, Kleist, Apr. 3, 1945; 2,531,571, Hyde. Nov. 28, 1950; 2,562,500, Lunt et al., July 31, 1951; and 2,616,165, Brennan, Nov. 4, 1952.

## Sheet and Plate Glass

*Apparatus for Grinding and/or Polishing Glass Sheets. Patent No. 2,767,522.* Filed December 1, 1954. Issued October 23, 1956. Two sheets of drawings; none reproduced. Assigned to Les Glaceries de la Sambre, Society Anonyme, by Edmond Laverdisse.

The present invention concerns the mounting of the tools for grinding and polishing glass, and relates more particularly to machines in which such tools are supported by beams, some of which are mounted above and some below the glass so as to act successively on the two faces thereof, or which are disposed in successive pairs to act simultaneously on the two faces of the glass.

Each horizontal coupling shaft is connected on the one hand to the vertical tool-carrying shafts by kinematic linkages, preferably of the rack-and-pinion type, and on the other hand to the beam by its bearings, in such manner that the movements of the tool-carrying shafts in relation to the beam in the vertical direction are made dependent upon the rotation of the horizontal coupling shaft. The latter may be rotated by a driving motor to raise the coupled tool-carrying shafts at will for the purpose of adjusting the working plane of the tools.

The tool-carrying shafts may in addition be connected together by a suspension cross member which is subjected to the action of the device for adjusting the working pressure of the tools on the glass. This cross member may, if desired, carry the bearings for the horizontal coupling shafts and thus be guided parallel to itself by the said shafts and their connections to the beam, without being engaged in slideways.

There were seven claims and the following references cited in this patent: 1,598,763, Evans, Sept. 7, 1926; 1,732,695, Platt, Oct. 22, 1929; 1,735,656, Drake, Nov. 12, 1929; 2,285,318, Waldron, June 2, 1942; 2,673,424, Laverdisse, Mar. 30, 1954; and 2,690,034, Laverdisse, Sept. 28, 1954.

*Method of Making Glass-to-Metal Seal. Patent No. 2,768,475.* Filed November 28, 1952. Issued October 30, 1956. Two sheets of drawings; none reproduced. Assigned to Radio Corporation of America, by H. R. Seelen and W. E. Anthony.

The present invention relates to improvements in the art of making an hermetic seal between a metallic frame member and one or more glass sheet-like members.

Multiple glazed insulation units heretofore have been unsatisfactory primarily because of failure of the air tight bond between the panes, as well as inability to withstand physical and thermal shock.

In accordance with the present invention, after the preglazing of the metal, additional frit is applied to the frame member so that, when the glass member is sealed to the frame, the additional frit fills in gaps between the glass member and the frame, making a continuous seal between them. Because the frame is shrunk onto the glass, a compression type hermetic seal results. Units so constructed, that is, with a continuous frame and using compression type glass-to-metal seals made in accordance with the present invention, can withstand greater physical and thermal shock than prior art multiple glazed units. Also, if the frit used in making the seal has a lower melting point than the glass, the seal may be made with little or no distortion of the glass member, since the glass need not be heated to its softening point in order for the sintered or molten frit to bond thereto.

There were eight claims and the following references cited in this patent: 2,122,453, Clause, July 5, 1938; 2,137,424, Thomas, Nov. 22, 1938; 2,151,809, Shardlow, Mar. 28, 1939; 2,558,878, Richardson, July 3, 1951; 2,589,064, Drake, Mar. 11, 1952; 2,625,717, Wampler et al., Jan. 20, 1953; 2,629,093, Pask et al., Feb. 17, 1953; and 578,580, Great Britain, July 3, 1946.

*Method of Producing Mirrors. Patent No. 2,770,558.* Filed December 13, 1952. Issued November 13, 1956. One sheet of drawings; none reproduced. Assigned to Libbey-Owens-Ford Glass Company by Romey A. Gaiser.

Generally speaking, the reflecting coatings on the mirrors of this invention are extremely thin films of materials having a higher refractive index than the base or mirror plate to which they are applied. For example, they may be films of tin oxide having a thickness of the order of one-quarter wave length of that portion of the visible spectrum to which the human eye is most sensitive (around 5600 Angstroms) on a vitreous substance such as glass.

The film of tin oxide may be applied to the surface of the glass by first heating the glass to a predetermined temperature then exposing it to the action of a suitable tin compound for a sufficient length of time to form a clear, transparent, relatively high reflecting coating, and discontinuing the treatment before a noticeable fog or objectionable color appears.

Excellent results have been obtained by spraying glass heated to 800° F. with a solution of anhydrous stannic tetrachloride in isopropyl alcohol. A solution of one part stannic tetrachloride in nine parts of isopropyl alcohol by volume is very satisfactory, but ranges of one to 50 parts of the tin chloride to 19 to 50 parts of the alcohol can also be used.

In spraying the sheet with the solution of the tin compound, it is important that care be taken to produce a uniform film. Spraying is continued until a film of the desired reflection characteristics is obtained and the spraying should be stopped before objectionable color appears. As a practical matter, this can be done visually by a trained operator. However, photoelectric cells connected with suitable recording instruments can be used, if desired, to measure the film as it is being applied, and to indicate when the desired thickness is attained.

With a glass mirror plate at a temperature of 800 degrees Fahrenheit and using a 10 per cent solution of stannic tetrachloride in isopropyl alcohol, a film having a thickness of one-quarter wave length of yellow green light around 5600 Angstroms will be deposited in from 8 to 10 seconds.

There was one claim and the following references cited in this patent: 2,118,795, Littleton, May 24, 1938; 2,394,533, Colbert et al., Feb. 12, 1946; 2,412,496, Dimmick, Dec. 10, 1946; 2,429,420, McMaster, Oct. 21, 1947; 2,430,452, Colbert et al., Nov. 11, 1947; 2,430,520, Marboe, Nov. 11, 1947; 2,439,654, Gaiser et al., Apr. 13, 1948; and 2,478,817, Gaiser, Aug. 9, 1949.

## Tube and Cane Machines

*Method of Making Glass-to-Metal Seals. Patent No. 2,786,307.* Filed May 18, 1953. Issued Mar. 26, 1957.

One sheet of drawings; none reproduced. Assigned to Owens-Illinois Glass Company by Leslie F. Pither.

The invention comprises the use of $SO_2$ during the fusing operation. The $SO_2$ may be mixed with the fuel gas wherein the fuel and $SO_2$ are mixed together and carried to a burner header.

The glass powder which is used in the coating is preferably of the same composition as the glass to which the metal contact button is to be sealed. The composition of the powder may, however, be different providing the expansion characteristics of the glasses are compatible to produce a substantially stress-free glass-to-metal seal, in accordance with generally accepted principles.

The vehicle, which is used in the coating solution, preferably contains a suspending agent for maintaining the glass particles in suspension and a binding agent for temporarily binding the glass particles to the metal until the glass may be fused to the metal.

The following are representative examples of glass-to-metal seals wherein the invention may be used and is of importance.

Metal—Sylvania No. 4 alloy (Patent No. 2,394,919):

| | |
|---|---|
| Nickel | 42 per cent |
| Chromium | 4-8 |
| Manganese | .25 |
| Iron | Balance |

Glass—Corning G-12:

| | |
|---|---|
| Silica ($SiO_2$) | 56.7 |
| Lead oxide (PbO) | 29.5 |
| Alumina ($Al_2O_3$) | 1.4 |
| Calcium oxide (CaO) | .1 |
| Sodium oxide ($Na_2O$) | 4.2 |
| Potassium oxide ($K_2O$) | 8.0 |
| Magnesium oxide (MgO) | 0.1 |

In coating anode buttons, a satisfactory vehicle consists of a solution of alcohol, water, and a resinous gum. The amounts of the various constituents in the vehicle are adjusted in order to provide a satisfactory and workable solution. A typical spray vehicle may have the following composition:

1,000 cc. distilled water
1,000 cc. alcohol
50 cc. resinous gum

The use of $SO_2$ gas during the fusing of the glass coating on an oxidized metal part prior to its being sealed with glass results in the elimination of minute bubbles, pin-holes, and in a more even edge on the coating. By thus providing a better glass coating, not only is subsequent overoxidation of the metal prevented but in addition a stronger seal is obtained by elimination of the points of weakness which might be caused by minute bubbles, pin-holes, or unevenness of the edge of the coating.

There were four claims and the following references cited in this patent: 2,254,945, Hunt et al., Sept. 2, 1941; 2,300,454, Lucas, Nov. 3, 1942; 2,301,741, Morris, Nov. 10, 1942; 2,542,043, McIntyre, Feb. 20, 1951; 2,596,694, Kegg, May 13, 1952; 2,629,093, Pask et al., Feb. 17, 1953. Other references: "Enamels," Andrews, Twin City Printing Company, pp. 300-302, First ed. (1935); "Manual of Porcelain Enameling," Hanson, Enamelist Publishing Company, pp. 384-387 (1937).

## Miscellaneous Processes

*Plastic Polishing Runner. Patent No. 2,757,491.* Filed January 16, 1953. Issued August 7, 1956. Two pages drawing; none reproduced. Assigned to Pittsburgh Plate Glass Company, by William F. Galey.

It has been discovered that the beneficial characteristics of felt polishers may be obtained without the inclusion of the undesirable properties of felt by the substitution of certain thermoplastic elastomers for use in forming polishing faces having high abrasion resistance. These polishing faces are formed of suitable shapes to form ridges and grooves, thereby enabling the ridges to impart a squeegee action to the surface of glass being polished.

Among the substances most suitable for use as polishers are certain polyvinyl halides such as polyvinyl chloride, vinyl chloride-fluoride copolymers, vinyl chloride-acetate copolymers, polyvinyl acetal, formal, propanal, butyral and polymerized mixtures of one or more of the latter. Also suitable are polyethylene and tetrafluoroethylene polymers such as Teflon. Additional suitable compounds are styrene copolymers, styrene elastomers such as "Styraloy," and copolymers of vinyl compounds with styrene polymers, for example butadiene-styrene copolymers vulcanized to improve their abrasion resistance. Other types of organic materials are also suitable for use as polishers such as silicone elastomers, thiokol, neoprene, and butyl rubber. In addition, Saran (polyvinylidene chloride), acrylonitrile resins which have been treated to improve their abrasion resistance and certain cellulose materials which are blended or plasticized with polyvinyl acetates are also suitable for use in forming the polishing runners provided they are suitably treated by either vulcanization, blending or plasticizing to form an organic compound provided with the desired characteristics.

---

## CONSUMERS GLASS, MONTREAL, ELECTS NEW OFFICERS

At a recent directors meeting of Consumers Glass Company Limited, Montreal, Canada, E. J. Brunning, president of the company since 1939, was elected chairman of the board. J. N. Jordan, vice president and general manager of the company, was elected president and general manager.

Mr. Jordan received his degree in engineering from McGill University in 1923 and joined the company in 1926. He was appointed works manager in 1939, vice president in charge of operations in 1951, and is currently a director of the company.

At the same meeting, C. G. Kemp was elected vice president in charge of operations. Mr. Kemp had joined the company in 1934 and has been works manager since 1951. He holds membership in the Engineering Institute of Canada and the Professional Engineers of Quebec.

• The appointment of William J. Collins as manager of metallurgy at Corning Glass Works was announced recently by the company. He replaces Roland E. Groethe who has resigned to join Jessop Steel Company at Washington, Pa.

Mr. Collins is a native of Charleroi, Pa., and originally joined Corning Glass Works in 1948.

# Research Digest

## Bonded Mullite and Zircon Refractories for the Glass Industry

• DESTRUCTION OF REFRACTORIES in glass melting furnaces is due to a combination of many factors, such as: (1) composition of raw batch and glass, (2) operating temperature, (3) rate of production or "pull," (4) furnace atmosphere and pressure, (5) gas velocity, (6) concentration of fluxes in gases, (7) composition and physical structure of the refractory, and (8) crystalline structure of the refractory.

The type and amount of fluxes present in furnace gases probably have the greatest effect on furnace upperstructure refractory. Batch dust containing fluxes of soda, lime, lead, potash, magnesia and boron seems most destructive. Improvements in batch charging and fritting, wider ports and regenerators, and reduced gas velocity have all helped reduce batch carry-over into the ports and checkers, resulting in improved refractory life.

There is no special refractory available which is not attacked by molten glass and/or furnace fluxing agents. Each material has its limitations and a careful selection of different refractories is necessary to obtain maximum furnace efficiency and economy.

Many super-refractories are available today and are used singly or in combination with other refractories to reinforce the more critical areas in melting furnaces. Super-refractories are generally made from minerals which may be calcined, sintered or electrically fused to make raw materials, either synthetic or natural, from which finished refractories are made. Many commercial refractories are entitled to the classification as "super-refractories"; among these are mullite and zircon materials.

It is these two types that are discussed by Knauft, Smith, Thomas and Pittman in the November 1957 issue of the *American Ceramic Society Bulletin.*

Mullite may be defined as "a refractory product consisting predominantly of mullite crystals ($3Al_2O_3.2SiO_2$) formed either by conversion of one or more of the sillimanite group of minerals or by synthesis from appropriate materials employing either melting or sintering processes."

The mullite grain and fabricated mullite refractories are composed of three constituents: mullite, alpha alumina, and glassy phase (cementing and interstitial).

The actual mullite content is the prime factor in determining the value and quality of a refractory in this field. Good refractories of the unfortified type will range from 82 to 93 per cent, averaging about 85 per cent mullite. Fortified types with addition of pure alumina, will contain 70 per cent or more mullite. Addition of the alumina depresses mullite formation during manufacturing; however, additional mullite is developed in service at high temperatures.

The glassy phase, both cementing and interstitial, may destroy or impair the properties that normally are the chief advantages of mullite when compared with other aluminum-silicate refractories. The cementing glass offers avenues for penetration of alkaline fluxes which dissolve the glass, and attack the interstitial impurities and finally the mullite crystals themselves as penetration is deeper. If the glass content is low, or is highly siliceous and viscous, fluxes attack the surface and form a porcelainitic interface which blocks further penetration.

Standard mullites should not contain more than 15 per cent glass, and usually average about 9 per cent. If the glass content is near the upper limit, it must be highly siliceous and viscous; otherwise, low melting eutectics develop causing vitrification and poor resistance to load at high temperatures. Fortified grades of mullite average about 7 per cent glass.

For a number of years, bonded mullite refractories have been extensively used in glass melting furnaces, primarily for furnace upperstructure, port and regenerator walls, and complete forehearths. Mullite super-refractories have the hot strength of silica brick without the tendency to spall when subjected to thermal shock; the softening point is 200° to 300°F. above the best grades of silica and fireclay brick; they are volume stable at high temperature; have low thermal conductivity, and are inert to either reducing or oxidizing atmospheres.

The mineral zircon was originally imported from Australia and India, where it was concentrated in alluvial deposits of beach sand. Since 1945, however, the unlimited beach sands of Florida have been the chief source of supply for domestic consumption. The zircon sand is associated with other minerals such as rutile, kyanite, garnet, monazite, sillimanite, and ilmenite and is recovered by flotation, magnetic, and electrostatic separation.

Zircon is an acid refractory and is more resistant to acidic glasses such as opal and boro-silicate than it is to flint, lead, and other basic glasses. Alkalies such as soda ($Na_2O$) react with zircon to form monoclinic zirconia and a sodium silicate glass. Silica brick and siliceous washes have but little effect on zircon; however, the presence of alumina in the wash can be very destructive. A binary eutectic composed of 80 per cent zircon, 20 per cent alumina melts at cone 31 (3050°F.); a ternary eutectic of 70 per cent silica 15 per cent zircon, and 15 per cent alumina fuses at cone 27 (2921°F.) and additional alkalies would lower the melting point appreciably. Thus it is necessary to protect zircon applications from aluminous washes and slags.

Both silica and aluminum-silicate refractories are readily attacked by the batch dust and vapor in glass tanks. Zircon has shown remarkable resistance to both silica wash and reaction with batch dust and vapor; crown washing does not attack zircon to any appreciable extent. Several opal furnaces now are using complete zircon upper-structure.

Improved sidewall flux blocks have developed considerable interest among glass plant operators for better bottom refractories. This is particularly true in opal furnaces where fusion cast sidewalls may last 3 to 3½ years, but clay bottoms will last only 12 to 16 months.

A preliminary trial of several bonded zircon sidewall blocks showed exceptional resistance to glass corrosion, with the resultant decision to install full 12 in. bonded, grog-type zircon bottom blocks for both melter and refiner.

Bonded zircon bricks have low thermal conductivity, are free from voids, and are uniform in size and dimension. The low thermal expansion eliminates the necessity for providing for expansion when installing zircon paving over old or new clay flux, and the use of zircon mortar for bonding gives tight joints which prevent penetration and upward drilling.

Bonded zircon refractories are not recommended as a substitute for either vacuum cast clay or fused cast blocks in the sidewalls of furnaces in which soda-lime container glasses are melted.

Zircon paving has also proved very satisfactory in special boro-silicate glasses. A section of the melter bottom, in a shallow end-fired furnace, was paved with 3 in. dry pressed zircon brick and 4 in. of fused cast blocks during a shutdown for minor repairs. Ten months later, the furnace came down for major repair and all paving was in excellent condition, with negligible loss.

Results to date in approximately 50 complete or partial installations, melting various types of glass, have shown zircon paving to be practical and economical when it is necessary or desirable to use a refractory other than clay bottom blocks in order to balance the furnace bottom with potential life of the sidewalls and other parts of the furnace.

With improved design and longer furnace life, feeder forehearths have necessarily required better refractories for production of high quality glass for extended campaigns. With glass temperature at the spout approaching 2500°F. on some types of glass, the expendable tubes, rings, plungers, and spouts have become more important in contributing to the hourly production and pack. These refractories must be able to retain dimension and shape in order to provide control and eliminate weight variation in the gob or drop at the orifice ring. They must also have high refractory properties and excellent resistance to glass corrosion and to thermal shock when replacing these expendable items.

Many types of refractories have been used for feeder forehearth construction, but the trend in recent years has been to use more super-refractories of the bonded mullite, fusion cast, zircon, and kaolin types. Improved glass quality from reduced stones, cords, seed, and blisters, as well as reduced iron streaking more than justifies the increased cost of using these types of refractories.

Bonded mullite and/or zircon refractories will not drip, and since they are low in iron, any glass which condenses on the exposed faces of the refractory, above the metal line, will remain relatively clean. With ordinary refractories, the stalactites found on the hot face are usually stained a greenish brown, from iron oxide in the refractory. Such drips melt and may be found in the ware as tadpoles.

Bonded zircon refractories have been quite successfully used in feeder forehearths, for channels, upper-structure, spouts, and orifice rings in melting operations involving dense opal and boro-silicate glasses.

During the recent months, a newly developed thermal-shock resistant zircon body has shown outstanding results when used for feeder tubes and plungers, in melting of dense opal and boro-silicate glasses. The corrosion resistance of zircon feeder parts has long been known, due to experience with spout and orifice rings, but previous compositions would not withstand the thermal shock involved in the hot replacement of feeder tubes and plungers. With normal preheating, operators are now able to install these successfully without cracking, and this special refractory body is highly regarded in several plants where it has been tested. Results indicate the life to be three to four times the life normally obtained when using bonded mullite and/or special clay composition parts.

---

J. G. King

## HAZEL-ATLAS NAMES J. GORDON KING

The appointment of J. Gordon King as general manager of its Hazel-Atlas Glass Division was announced recently by Continental Can Company. Mr. King, formerly a vice-president of Owens-Illinois Glass Company, brings to his new position a lifetime of experience in the glass industry. He will make his headquarters in Wheeling, West Virginia.

Mr. King succeeds Howard G. Lewis who has retired at his own request after more than a quarter century of service with Hazel-Atlas.

## JOSEPH LOCKE COLLECTION ESTABLISHED AT ALFRED U.

The Joseph Locke Memorial Collection has been established at Alfred University with the presentation of 15 pieces of art glass to the University by Mrs. Robert A. Williamson of Pittsburgh, Locke's only surviving daughter.

Before his death in Pittsburgh in 1936, Locke was regarded as an outstanding artist in the field of glass. Many of his pieces are internationally famous. Born in England in 1846, Locke lived 52 years in the United States.

The 15 pieces forming the new collection which will be permanently exhibited in State University of New York College of Ceramics at Alfred University, were obtained through the assistance of Dr. Alexander Silverman and the generosity of Mrs. Williamson. Dr. Silverman, professor of chemistry emeritus at the University of Pittsburgh, is himself distinguished as a collector of glass and was a personal friend of Locke.

Mrs. Williamson allowed Dr. Silverman and Mrs. Daniel Rase of the College of Ceramics to choose the 15 pieces which best illustrated the outstanding qualities of her father's work. Mrs. Rase is curator of the Alexander Silverman Glass Collection at Alfred University. The principal pieces selected are vases, pitchers, and glasses.

# Current Statistical Position of Glass

**Employment and payrolls:** Employment in the glass industry during December, 1957 was as follows: *Flat Glass*: A preliminary figure of 29,400 has been given for December, 1957, which is identical to the adjusted figure reported for November, 1957. *Glass and Glassware, Pressed and Blown*: A decrease of 4.4 per cent is shown by the preliminary figure of 78,300 given for December, 1957, when compared with the adjusted figure of 81,900 given for November, 1957. *Glass Products Made of Purchased Glass*: The preliminary figure of 13,500 listed for December, 1957 is exactly the same as the previous month's adjusted figure.

Payrolls in the glass industry during December, 1957 were as follows: *Flat Glass*: A decrease of 6.6 per cent is shown in the preliminary $15,107,203.82 for December, 1957 when compared with November's adjusted figure of $16,172,185.89. *Glass and Glassware, Pressed and Blown*: A decrease of 5.5 per cent is shown in the preliminary $28,627,930.68 reported for December, 1957 when compared with the previous month's adjusted $30,277,738.76. *Glass Products Made of Purchased Glass*: A preliminary figure of $3,840,970.63 was reported for December, 1957. This is a decrease of .2 per cent when compared with the adjusted figure of $3,848,964.00 from the previous month.

**Glass container production:** Production based on figures released by the Bureau of the Census was 11,714,000 gross during January, 1958. This represents an increase of 9.4 per cent from the previous month's production of 10,705,000 gross. During January, 1957, glass container production was 11,698,000 gross or .9 per cent below the January, 1958 figures.

Shipments of glass containers during January, 1958 came to 10,879,000 gross, or an increase of 14.6 per cent over the December, 1957 shipments, which were 9,494,000 gross. Shipments during January, 1957 were 10,312,000 gross or 5.5 per cent lower than January, 1958.

Stocks on hand at the end of January, 1958 came to 18,051,000 gross. This is 4 per cent above the 17,352,000 gross on hand at the end of December, 1957, and 20.5 per cent higher than the 14,976,000 gross on hand at the end of January, 1957.

## GLASS CONTAINER SHIPMENTS

(All Figures in Gross)

| | Jan., 1958 |
|---|---|
| **Narrow Neck Containers** | |
| Food | 941,000 |
| Medicinal and Health Supplies | 1,469,000 |
| Chemical, Household and Industrial | 804,000 |
| Toiletries and Cosmetics | 732,000 |
| Beverage, Returnable | 801,000 |
| Beverage, Non-Returnable | 93,000 |
| Beer, Returnable | 62,000 |
| Beer, Non-Returnable | 520,000 |
| Liquor | 601,000 |
| Wine | 364,000 |
| Sub-total (Narrow) | 6,387,000 |
| **Wide Mouth Containers** | |
| Food | *3,214,000 |
| Medicinal and Health Supplies | 442,000 |
| Chemical, Household and Industrial | 143,000 |
| Toiletries and Cosmetics | 248,000 |
| Packers' Tumblers | 58,000 |
| Dairy Products | 152,000 |
| Sub-total (Wide) | 4,257,000 |
| Total Domestic | 10,644,000 |
| Export Shipments | 235,000 |
| TOTAL SHIPMENTS | *10,879,000 |

* This figure includes Fruit Jars and Jelly Glasses.

## GLASS CONTAINER PRODUCTION AND INVENTORY

(All Figures in Gross)

| | | Production Jan., 1958 | Stocks Jan., 1958 |
|---|---|---|---|
| Food, Medicinal and Health Supplies; Chemical, Household and Industrial; Toiletries and Cosmetics | Narrow Neck | 4,200,000 | 6,572,000 |
| | Wide Mouth | *4,273,000 | *5,587,000 |
| Beverage, Returnable | | 1,040,000 | 1,923,000 |
| Beverage, Non-Returnable | | 129,000 | 250,000 |
| Beer, Returnable | | 189,000 | 417,000 |
| Beer, Non-Returnable | | 599,000 | 795,000 |
| Liquor | | 618,000 | 1,424,000 |
| Wine | | 421,000 | 702,000 |
| Packers' Tumblers | | 61,000 | 83,000 |
| Dairy Products | | 184,000 | 298,000 |
| TOTAL | | *11,714,000 | *18,051,000 |

* This figure includes Fruit Jars and Jelly Glasses.

## RUTGERS U., SCHOOL OF CERAMICS, RECEIVES ADDITIONAL GRANT

Expressing great satisfaction with results already accomplished at the School of Ceramics, Rutgers University, on the use of lead compounds in ceramic bodies under a grant made by the Lead Industries Association last year, Robert L. Ziegfeld, Association secretary, has announced a new grant to Rutgers which will more than double the funds available for the work this year. It is under the direction of Dr. John H. Koenig, director of the School of Ceramics.

## CORNING ANNOUNCES APPOINTMENTS

Two appointments in the Mechanical Engineering Department of Corning Glass Works were announced recently by the company.

George E. Watkins was appointed manager of Machinery Development Department No. 1. This department will normally do the design and development work for machinery required by the television, bulb and tubing plants of the company.

Alvah J. Dorn was appointed manager of Machinery Development Department No. 2. This department will normally do design and development work for presses, apparatus and consumer products machines.

# New Equipment and Supplies

## NEW BURETTES WITH AUTOMATIC ZERO

Scientific Glass Apparatus Company, Inc., Bloomfield, New Jersey, announces the development of two new burettes with automatic zero which require no lubrication and prevent frozen connections.

According to the company, the reason no lubrication is required and the connections cannot freeze is due to the fact that both the plug and the bushing are made of Teflon (Du Pont tetrafluorethylene). An added insurance against sticking and freezing is obtained through use of a patented process in which a special compound of chemical materials is applied to the ground surface on the inside of the barrel, into which the plug fits, and the neck of the reservoir, and then is fused at high temperature to form a bearing permanently bonded to the glass surface.

The company claims that the burettes are simple to operate. They are available in two styles: TJ-716 for acids and TJ-742 for alkali solutions. The latter has drying tubes at each opening to the air, filled with activated alumina for adsorption of vapors and moisture. An automatic air check valve is located within the side arm to which the rubber bulb is attached. The burette and reservoir are made of hard borosilicate glass. The graduated section is made of precision bore tubing. The easy-to-read graduations are accurate and meet National Bureau of Standards Circular C-434.

## LIQUEFIED GAS LEVEL-REGULATOR

Fisher Scientific Company, 498 Fisher Building, Pittsburgh 19, Pa., has designed a liquefied gas level-regulator. The glass instrument is said to maintain any desired level of liquefied gas, within a quarter of an inch, in the cold finger or freezing bath of any apparatus.

The device works with liquefied air or oxygen as well as with liquefied nitrogen. Once adjusted, it operates as long as there is a supply of liquid in the reservoir.

The Levilator is claimed to be ideal for cryoscopic investigations, mass spectrometry, vacuum distillations, freeze drying, and a host of other vacuum techniques; it operates without pumps, motors, or mechanical devices of any kind.

Made of Pyrex-brand glass, the device is essentially an "S"-shaped air thermometer with a sensing bulb at one end and a "breather" tube at the other. The breather end is filled with about 4 ml of mercury and connected with rubber tubing to the vent on the liquefied-gas reservoir. The sensing bulb is set at the desired level in the cold finger or the bath for the cold trap.

As the liquid in the bath or cold finger evaporates, its level drops. The air in the bulb grows warmer and expands, causing the mercury to rise and seal the breather tube. When the desired level of liquefied gas is reached again, the extreme cold reduces the volume of air in the sensing bulb. The mercury falls, and the reservoir breather opens again. With the pressure released, the liquid ceases to flow.

## FUSED QUARTZ IN SPECIAL SHAPES

Amersil Quartz Division, Engelhard Industries, Inc., 685 Ramsey Avenue, Hillside 5, N. J., now has available fused quartz which can be forged to special shapes. Quartz users, it is claimed, can eliminate up to 95 per cent of the wastage of this material. The firm announced that it now is prepared

to forge fused-quartz blanks to most customers' specifications. Among the shapes available in various sizes are rods, cubes, briquets, and prisms, as well as forged guided-missile domes shaped like scooped-out cantaloupe halves.

The company fuses its quartz by a new process which is said to produce more homogeneous material with less thermal strain and fewer and smaller bubbles. Such material can be forged—that is, reheated to a semi-molten or slushy state and squeezed into the desired shape. Conventionally processed fused quartz cannot take the strains produced by this operation, and the large bubbles within it are likely to grow even larger as a result of the reheating, according to Amersil.

## 20 INCH MASONRY SAW

Robert G. Evans Company, 6024 Troost Avenue, Kansas City 10, Mo., offers a masonry saw with a standard cutting head that will take 14, 18, or 20 inch blades. The shaft speed has been calculated so that it is never necessary to change belts or pulleys when switching from a blade of one diameter to a larger or smaller blade. Another feature is a precision-molded conveyor cart, which provides a replaceable insert that prevents sawing through, and guards the blade against damage. Further advantages are said to include a water reservoir that contains 38 per cent more water and keeps water more free of sludge, a new frame design for balanced weight, and a cutting head which affords a good weight reduction.

## HIGH TEMPERATURE ATMOSPHERE FURNACE

Lindberg Engineering Company, Pilot Plant Equipment Division, 2444 West Hubbard Street, Chicago 12, Ill., has announced a new high temperature vertical tube atmosphere furnace.

The unit is said to be ideal for numerous pilot plant or laboratory applications requiring protective atmosphere, cooling chamber and accurate stepless temperature control up to 2750°F. (1510°C.). The furnace is a self-contained unit with all electrical components in the bottom portion and is completely pre-wired and piped.

## CATALOGS RECEIVED

*Selas Corporation of America*, Dresher, Pa., has available two new bulletins; both are illustrated with photographs and diagrams. Order them direct from the company.

Bulletin SC-1013 describes the company's dehydrators, built to meet specific needs for effective and economical removal of moisture from most gases. Moisture removal and discharge from the system is continuous, with no flow interference. Gas inlet pressures may range from a few pounds gage to 150 psig for standard design, or up to 3500 or more psig for special applications.

Bulletin S-1055 discusses compact, lightweight laboratory furnaces which provide continuous or intermittent operating temperatures from 1000°F. (538°C.) to over 3350°F. (1844°C.) for testing or processing small samples. All are suitable for bench mounting and can usually be used without hood. Thick refractory lining and heavy steel jackets minimize heat loss, extend life, and assure comfortable working conditions.

*Wheelabrator Corporation*, 1026 S. Byrkit Street, Mishawaka, Ind., announces a new 32-page illustrated catalog, No. 951-D, covering the company's entire line of airless blast cleaning machines as well as wet blast, air blast and dust control equipment. Also included are cast steel shot and grit abrasives, sandcutters and core rod straighteners.

Listed for the first time is a new line of heavy duty batch-type centrifugal blast cleaning machines.

**Here's why WEST END can answer an inquiry on your particular specifications immediately!**

When you require special data on a WEST END product and phone for information, the Sales Office Manager in Oakland with whom you speak can contact the plant at WEST END immediately. He talks by private wire teletype with the Technical Director and receives an authoritative answer immediately. It is relayed to you often while you are still on the phone.

WEST END 's Sales Office Manager sales representatives and plant executives work together as a team manning a system that is, in our opinion, uniquely outstanding in the chemical industry. Their confidence in the efficiency of this system is reflected in the enthusiastic, helpful and friendly manner in which they promptly serve you . . . our customers.

**WEST END CHEMICAL COMPANY**
DIVISION OF STAUFFER CHEMICAL COMPANY
1956 WEBSTER, OAKLAND 12, CALIF. • PLANT, WESTEND, CALIF.

**SODA ASH**
**SODIUM SULFATE**
**BORAX • HYDRATED LIME**

## J. B. SHIMER OPENS CONSULTING OFFICE

J. B. Shimer

Johnston B. Shimer, glass technician and chairman of the board of Oneida Machine Tool Corporation, has recently opened a technical consulting service at Sherwood Forest, Maryland. The consulting office will be administered as a specialized service for the glass and ceramic industries only.

Mr. Shimer's career as a glass technologist has been exceptional in that he has acquired a great variety of glass factory experience. After graduating from Lehigh University in 1929 with a degree in chemical engineering, he spent a year with E. I. duPont de Nemours and Company. This was followed by 15 years with Corning Glass Works, making scientific and technical glassware. During this period Mr. Shimer served in various capacities, from departmental work to the holding of plant managerships.

The next seven years were spent with Kimble Glass Company as factory manager, making television tubes and scientific glassware. Later, Mr. Shimer did special work for The Buck Glass Company while in charge of the company's factory in Baltimore. Until recently, he has been general manufacturing manager at Knox Glass, Inc. At present, Mr. Shimer is engaged in a special training study for The Buck Glass Company and others.

Mr. Shimer believes a consulting office should understand thoroughly the seriousness of conflicting relationships with clients. He feels that a consultant should never take on a specific technical problem directly affecting another client, who may have work being done on the same sort of project.

## M.I.T. COMPLETES SOLAR HOUSE

A unique full-scale sun-heated house, the first of its kind designed to meet modern living requirements, has just been completed by a Massachusetts Institute of Technology team of engineers and architects. Located in the suburban Boston community of Lexington, Mass., the two-story, three-bedroom house is also a pioneering attempt at using a hot-water solar-system in a full-scale home.

The result of 20 years of solar energy research at M.I.T., the house has been built to demonstrate that enough facts and equipment are now available to combine a reliably engineered solar heating system with a house designed for comfortable suburban living in a northern climate.

The house itself will be sold to a private family, but M.I.T. engineers will retain separate access to a basement equipment and instrument room to gather further data on the performance of the solar heating system after the purchaser has moved in.

The most striking feature of the house is, of course, its solar collector, the equipment by which the sun's energy is trapped for heating use. This consists of 640 square feet of glass, two layers thick, over a similar area of thin (.025 inches) aluminum sheet painted a heat-absorbing black. While the aluminum sheet absorbs the solar energy, the glass serves the same purpose it does in a green-house; it lets the sunshine in, but keeps the longer waves of heat energy from passing back out again.

## KNOX GLASS APPOINTS H. S. WAHLNER

In a move designed to create new operating efficiencies as well as to establish considerable cost savings in its yearly purchases, Knox Glass Incorporated has appointed Harold S. Wahlner to the position of general purchasing agent, according to Dr. Arthur W. Wishart, Knox president. All purchasing activities of the firm, except for emergencies such as shut-downs for furnace repair, will be centralized at the Knox, Pa., headquarters of the firm, the president said.

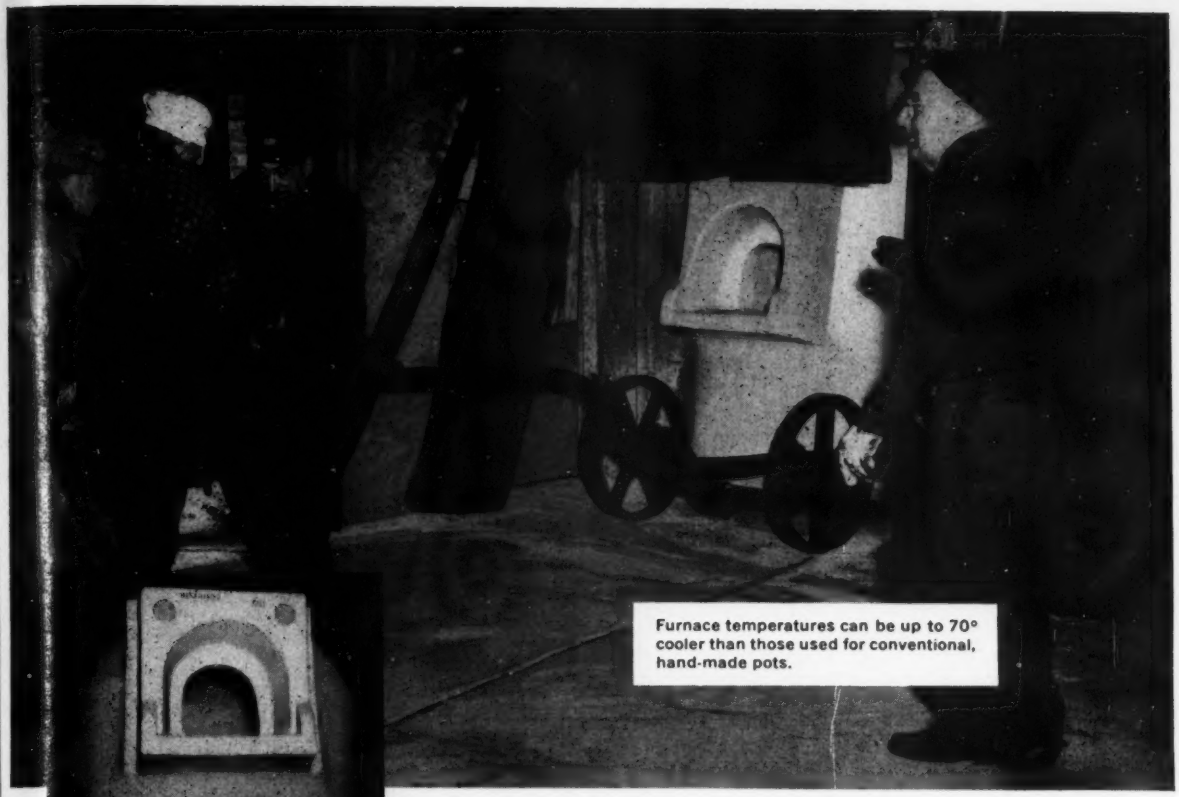
H. S. Wahlner

Previous company policy had permitted autonomous purchasing, under the general supervision of purchasing officers for the northern and southern divisions of the firm. Knox headquarters had controlled such activities for the plants at Knox, Marienville and Parker, all in Pennsylvania, and at Gas City, Indiana. Jackson, Mississippi, headquarters of the southern division had overseen activities for the two plants in that city and for the plant.

If individual plant managers are held responsible for their own inventories and for estimating yearly requirements in advance, considerable economies can be effected through quantity purchasing, according to Mr. Wahlner. Further, the company will establish better contacts with its suppliers, many of whom could not service each of the plants as efficiently as will be possible under the new procedures, he said.

Current expansion plans of the company have emphasized the necessity for closer controls. A new flint glass manufacturing plant and warehouse is being established at Danielson, Conn., and a new amber furnace has just been installed at the Palestine, Texas, plant. Automated batching facilities are being constructed at Gas City, Indiana, and additional warehousing areas are to be added at several other plants.

Mr. Wahlner, a veteran of the glass container manufacturing industry, was formerly assistant purchasing agent for a large competitive company. He gained experience in both the cold and hot ends of manufacturing before going into the company's headquarters office. After several years in the accounting department, he was promoted into the purchasing department.



Furnace temperatures can be up to 70° cooler than those used for conventional, hand-made pots.

Great structural strength resists shock of shipping and heavy handling.

# *Viking Glass Sets Record:*

# 180 MELTS FROM A LACLEDE-CHRISTY POT!

This remarkable record was set between November, 1955 and August, 1957 at the Viking Glass Company plant in New Martinsville, West Va. It's especially significant because *three kinds of glass* were processed in this same pot: flint glass, and two different colored varieties.

**SALEABLE GLASSWARE** increases notably when a Laclede-Christy 100% cast melting pot is installed. Contaminated glass is minimized. Fuel savings are substantial. And Laclede-Christy pots take on furnace temperatures during preheating without cracking.

**LONG LIFE,** 100% cast glass pots—made *exclusively* by Laclede-Christy—are designed to help you make better glass, at less cost. Investigate this *modern* melting pot. Contact your local field representative for information. He's in the Yellow Pages, under "Refractories". Or write to *Laclede-Christy Works, Refractories Division, H. K. Porter Company, Inc., St. Louis 10, Mo. In Canada, H. K. Porter Company (Canada) Ltd., Guelph, Ontario.*

## H. K. PORTER COMPANY, INC.

REFRACTORIES DIVISION

Connors Steel, Delta-Star Electric, Disston, Forge and Fittings, Leschen Wire Rope, Quaker Rubber, Refractories, Riverside-Alloy Metal, Vulcan Crucible Steel, H K. Porter Company (Canada) Ltd.

**Spectra of Simple Glasses . . .**
(*Continued from page* 154)

sure of the sample at the same temperature brought about the inversion of the α-modification into the β-form (curve e). The spectrum of the central core of the glass after 12 hours of exposure was neither similar to the spectrum of the initial glass nor to the spectrum of the crystallized part of it. It is distinctly divided into two parts. Silica, together with a certain new silicate which has the minimum of transmission at 10.40 μ, was inclined to segregate. In the series of the crystallized glasses of sodium disilicate composition the maximum at 10.4 μ is distinctly developed in the reflection spectrum, but is absent in some other glasses.

In the spectrum of a film blown from the glass melt an intense maximum is observed at 10.4 μ as shown above. To which silicate this minimum may belong remains unknown at the present time. The principal bands of the known silicates and crystalline solutions investigated by us in the crystallization products of glasses with 15 to 67 molec. per cent $Na_2O$ are lying at different wave lengths.

From all of the facts here discussed it follows that in the formation of the structure of sodium silicate glasses silica participates together with a series of silicates (the complete detection of which, however, is not easy).

## SUMMARY

On the basis of the material discussed we may draw the following conclusions:

1. The thermal history of a glass from its melt to the solid state and the subsequent crystallization may be traced by analyzing the structure of the glass using infrared radiation methods.

2. The microstructure of glass is complex and heterogeneous; silica, in different modifications, and silicates participate in its formation, the latter appearing as distinct chemical compounds and also as crystalline solutions.

3. There are zones with a regular structure in the glass, i.e. crystallites exist with atomic positions similar to those in the crystals of the silica modifications and corresponding silicates. There is a continuous transition from the most regular parts of these zones to irregular portions, and vice-versa to order in neighboring crystallites. The formation of groups from which crystallites are formed in the cooling glass begins very early, even in a glass melt above the Liquidus temperature. The diameters of the crystallites are evidently somewhat larger than those indicated by the X-ray analysis.

4. The [$SiO_4$] tetrahedra in the glass are discussed as formations which have variable, not definite distances between the silicon and oxygen atoms. The average distances are smallest in silica glass, and largest in glasses with isle structures.

## BIBLIOGRAPHY

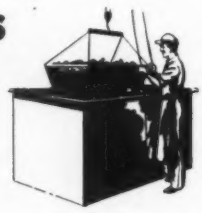
(15) A. Ya.Kuznetsov and I. G. Mel'nikova, *Zhurn. Fiz. Khim. 24.* 1950, 1204-1209. Chem. Abstr. *45*, 1951. 5381 i.
(16) K. S. Evstropev and M. M. Skornyakov, Phys.-Chem. Properties of the Ternary System $Na_2O$ - PbO - $SiO_2$. Sbornik, Izd. A.N.S.S.S.R. 1949. 174-185; Chem. Abstr. *46*, 1952. 10831 f, h.
(17) B. E. Warren and J. Biscoe, *J. Amer. Ceram. Soc. 21.* 1938. 259-265. B. E. Warren and A. D. Loring, *ibid. 18.* 1935. 269-276.
(18) M. F. Vuks and V. A. Ioffe, Phys.-Chem. Properties of the Ternary System $Na_2O$-PbO-$SiO_2$. (Sbornik) Izd. Akad. Nauk S.S.S.R. 1949. 164-173; Chem. Abstr. *46*, 1952. 10831 e.
(19) E. F. Gross and V. A. Kolesova, Zhurn. Fiz. Khim. *26.* 1952. 1673-1680; Chem. Abstr. *47*. 1953. 6254 d.

## ACKNOWLEDGEMENT

The translator is much indebted to Mr. Stephen W. Barber, Technical Center, Owens-Illinois Glass Company, Toledo, Ohio; to Dr. Marianus Czerny, Institute of Physics, University of Frankfurt am Main, Germany; to Dr. W. D. Keller, Department of Geology, University of Missouri, Columbia, Mo.; and to Dr. E. E. Pickett, Spectrographic Laboratories, University of Missouri, Columbia, Mo., for their valuable help and advice in examining the text of the present translation. My sincere thanks are also due for the most fascinating discussions and exchange of opinion in the correspondence on the interesting article of Miss Florinskaya and Miss Pechenkina in one of the most important fields of glass constitution research.

—W. E.

**Clean glass molds without scraping or sandblasting!**



Now, simply by soaking and rinsing, you can quickly remove heat scale, mold lubricants and carbon from steel molds used in producing bottles, jars, jugs and other items. Oakite specialized compounds do the job chemically. They work fast because of their outstanding ability to wet-out, dissolve and break up soils . . . emulsify oil, grease . . . rinse freely.

Talk to your local Oakite Technical Service Representative, or write for details to Oakite Products, Inc., 25C Rector Street, New York 6, N. Y.

SPECIALIZED INDUSTRIAL CLEANING
OAKITE
MATERIALS METHODS SERVICE
SCIENCE

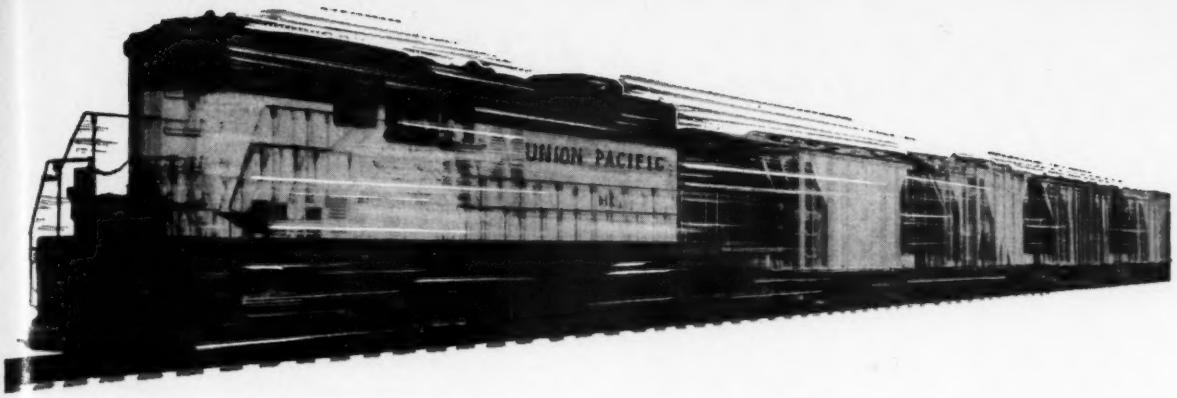
Export Division Cable Address: Oakite

Technical Service Representatives in Principal Cities of U. S. and Canada

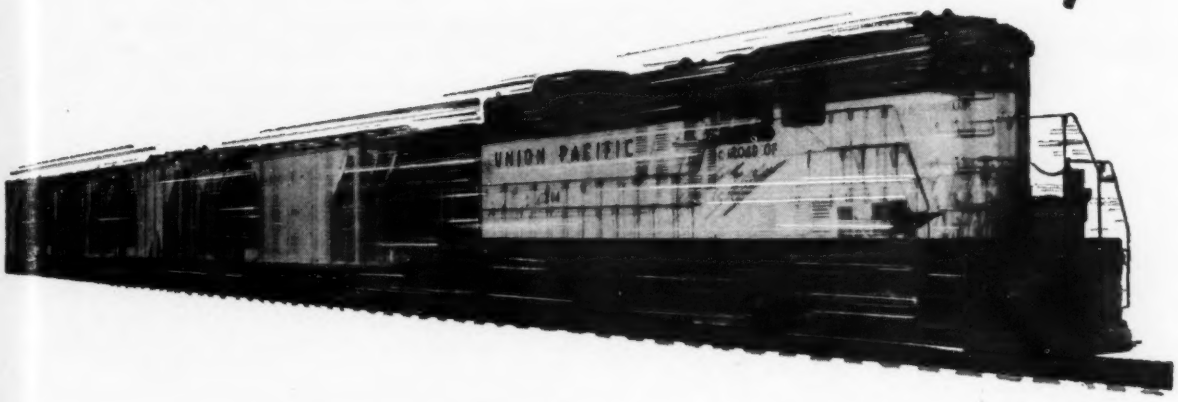
## W. M. TROUTMAN IS VICE PRESIDENT OF GENERAL REFRACTORIES

Ward M. Troutman, Pittsburgh district sales manager for the General Refractories Company, has been named vice president of the company. His office will remain in Pittsburgh.

Mr. Troutman, joined General Refractories Company in 1947 as a member of the Pittsburgh district sales force. He was named assistant district sales manager in June 1953 and promoted to district sales manager in January 1954 Prior to coming with the company he was employed in the sales department of the Haws Refractories Company from 1938 until 1947, interrupted only by two years of Naval service.




you say *when and how many*




## Westvaco® Soda Ash is "delivered as promised" by America's largest hopper-car fleet!

Around the clock and around the calendar, some 300 Westvaco Soda Ash covered hopper-cars are in regular customer service. That's by far the largest fleet of modern cars in the industry. It's one more good reason why you'll be happy with Westvaco Soda Ash.

Other reasons?

Product quality—chemical and physical. Shipping specs held consistently between 99.75% and 99.88% so you get more $Na_2CO_3$ per gross ton. Low iron and other impurities that might discolor solids, mixtures or solutions. Fewer fines, less dusting. Free flowing for faster unloading and handling.

Increasing plant efficiency continues to make more Westvaco Soda Ash available for more users in our shipping area covering two-thirds of the United States. It's quite probable you can get premium quality Westvaco Soda Ash without paying one penny more.

Why not get our quotation on a fair share of your needs?

*Putting Ideas to Work*

FOOD MACHINERY AND CHEMICAL CORPORATION

**Westvaco Chlor-Alkali Division**

**General Sales Offices:**
**161 E. 42nd STREET, NEW YORK 17**

# Milestones in Glass Progress

PHOTO COURTESY OWENS-CORNING FIBERGLAS CORPORATION

*1937* Curtains and drapery materials made from glass have found great acceptance largely due to their inherent characteristics: they will not burn, shrink, sag, stretch, rot, or mildew. Easy to maintain because they resist dirt, they are water repellent, sunproof. Currently, over 100 varieties of these fabrics are in use.

*1890* Michigan Alkali Company, now a division of Wyandotte Chemicals Corporation, was founded by Captain I. B. Ford to supply Soda Ash to the glass industry. At Wyandotte, there is no compromise with quality — insured by rigid tests from arrival of limestone at our docks (above), to final delivery of Soda Ash. Another reason why Wyandotte is a dependable source of raw-material chemicals for glassmakers.

**Wyandotte CHEMICALS**

*Michigan Alkali Division, Wyandotte Chemicals Corporation*
*Wyandotte, Michigan • Offices in principal cities*

*Founded by a Glassmaker to Serve the Glass Industry*


## Use of Sulfates . . .

(*Continued from page* 142)

### SUMMARY

Sulfates are an important factor in fining rates of any given glass. Sulfate usage is the important key to controlling color of any given glass through control of oxidation reduction effects. An empirical method of estimating oxidiation-reduction influences is given. This data then must be altered to fit the melting unit in question. Once this is done it becomes a powerful tool to evaluate some of the unknowns remaining in the glass melting process.

The first application of a tool of this type serves only to evaluate the melting unit in question. Subsequent applications then become of more and more value as more knowledge is obtained about the melting unit in question.

### BIBLIOGRAPHY

(1) J. W. Wright, "Some Practical Aspects of Seeds and Fining" (a summary), *Glass Industry*, December, 1955.
(2) R. W. Hopkins and W. H. Manring, "Factors Influencing Control of Color in Amber Glasses", *Glass Industry*, May, 1953.
(3) R. K. Day, "Glass Research Methods", Industrial Publications, Inc., 1953.

## H. H. ROSENBERG, FOUNDER OF INDUSTRIAL PUBLICATIONS, DIES

A lifetime in publishing ended on February 24 with the death of Harold H. Rosenberg, age 75, chairman of the board and founder of Industrial Publications, Inc. Death occurred, after an extended illness, at Mt. Sinai Hospital in Los Angeles and interment was at Forest Lawn Memorial Park, Glendale, Calif. Mr. Rosenberg's permanent address was 14242 School Street, Ivanhoe, Ill.

Mr. Rosenberg was born in Liverpool, England in 1882; at the age of five he was brought to Chicago by his parents. He received his early education in the public schools of the city. He went to work at an early age, and held a variety of jobs until 1907 when he came to Kenfield-Leach Company, printers and publishers of trade magazines, as printing manager.

Soon after, Mr. Rosenberg became manager of one of the company's magazines, Brick, which later became Brick & Clay Record. It is still published by Industrial Publications, Inc. Mr. Rosenberg formed that company in 1920, serving as president and editor-publisher until 1954 when he assumed the position of chairman of the board. During the years, he established five of the eight publications which the company produces at this time.

## DIAMOND ALKALI EXPANDS MARKET RESEARCH

Diamond Alkali Company, Cleveland, Ohio is expanding the market research activities of its Commercial Development Department "to provide increased market research on existing products particularly for Diamond's seven operating divisions and its sales department," it was announced recently by C. A. Butler, Jr., director of commercial development.

The market research section of the Commercial Development Department, previously concerned principally with new products, is being enlarged to handle this new and broader assignment and will continue to be directed by George Rieger, chief of market research since April, 1955.

# STAR PERFORMERS

## ON THE ACL PRODUCTION LINE

Three brilliant stars in the star-studded BFD Series 19 bottle colors.

These enamels offer the finest qualities available for ACL printing. All are production proved. Convince yourself. Make trial runs in your own plant. For prompt delivery of samples, phone or write today.

**DEPENDABLE SERVICE ON:** Acid, Alkali and Sulphide Resistant Glass colors and Enamels...Silver Paste . . . Crystal Ices . . . Porcelain Enamel Colors . . . Body, Slip and Glaze Stains . . . Overglaze and Underglaze Colors . . . Squeegee and Printing Oils . . . Spraying and Banding Mediums . . . Metallic Oxides and Chemicals.

CALL ON *Drakenfeld*

*R PARTNER IN SOLVING COLOR PROBLEMS*

B. F. DRAKENFELD & CO., INC.

*Executive Offices:* 45 Park Place, New York 7, N. Y.

*Factory and Laboratories:* Washington, Pa.

*Pacific Coast Agents:*

BRAUN CHEMICAL COMPANY, 1363 So. Bonnie Beach Place
LOS ANGELES 54, California Phone: ANgelus 9-9311

BRAUN-KNECHT-HEIMANN COMPANY, 1400 Sixteenth Street
SAN FRANCISCO 19, California Phone: HEmlock 1-8800

THE
PENELECTRO
BUBBLER SYSTEM
FOR GLASS FURNACES

- *Improves Homogeneity*
- *Increases Output*
- *Lowers Seed Count*
- *Decreases Fuel Consumption*

**Another PENBERTHY**
**Glass Process Improvement**

Penberthy Electromelt Co.
SEATTLE 16, WASHINGTON
PEN ELECTRO
U. S. Pat. 2,883,488 OTHERS PENDING

PENBERTHY
ELECTROMELT COMPANY
4301 6th Ave. So., Seattle, Wash.

TOMOCO MOULDS

Assure You Of Trouble-Free, High Speed Production
On All Types Of

BOTTLES, JARS AND PRESSED TABLEWARE

40 years experience in this important phase of the glass industry have given us the know-how on which you can depend. A complete designing, engineering and manufacturing service.

PROMPT DELIVERIES

The Toledo Mould Co.

1923 Clinton St. Toledo 7, Ohio
CHerry 4-3066
*In The Glass Center Of The World Since 1918*

## GORDON RESEARCH CONFERENCES GLASS PROGRAM ANNOUNCED

The Gordon Research Conferences for 1958 will be held from June 9 to August 29 at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

The Conferences were established to stimulate research in universities, research foundations and industrial laboratories. The purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for participation in discussion groups as the individual desires.

Requests for attendance at the Conferences, or for any additional information, should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 9 to August 29, 1958 mail should be addressed to Colby Junior College, New London, New Hampshire. Attendance at each Conference is limited to 100.

---

The section dealing with glass at the Gordon Research Conferences will meet from August 25-29 at Kimball Union Academy, Meriden, N.H. James E. Archer is chairman and R. J. Charles, vice chairman. "Physiochemical Aspects of Glass" will be the general topic.

The program is as follows:

August 25:
- General Introduction
- R. W. Douglas. Transport Phenomena in Glasses
- Speaker to be announced. Thermodynamic Considerations of Glasses and Slags.

August 26:
- J. Ulys. Water in Silicate Melts.
- Panel Presentation. Room Temperature Reactivity of Glasses.

August 27:
- J. Gibbs. Nature of the Glass Transition in Linear Polymers.
- W. Hillig. Kinetic Stability of the Glassy State.

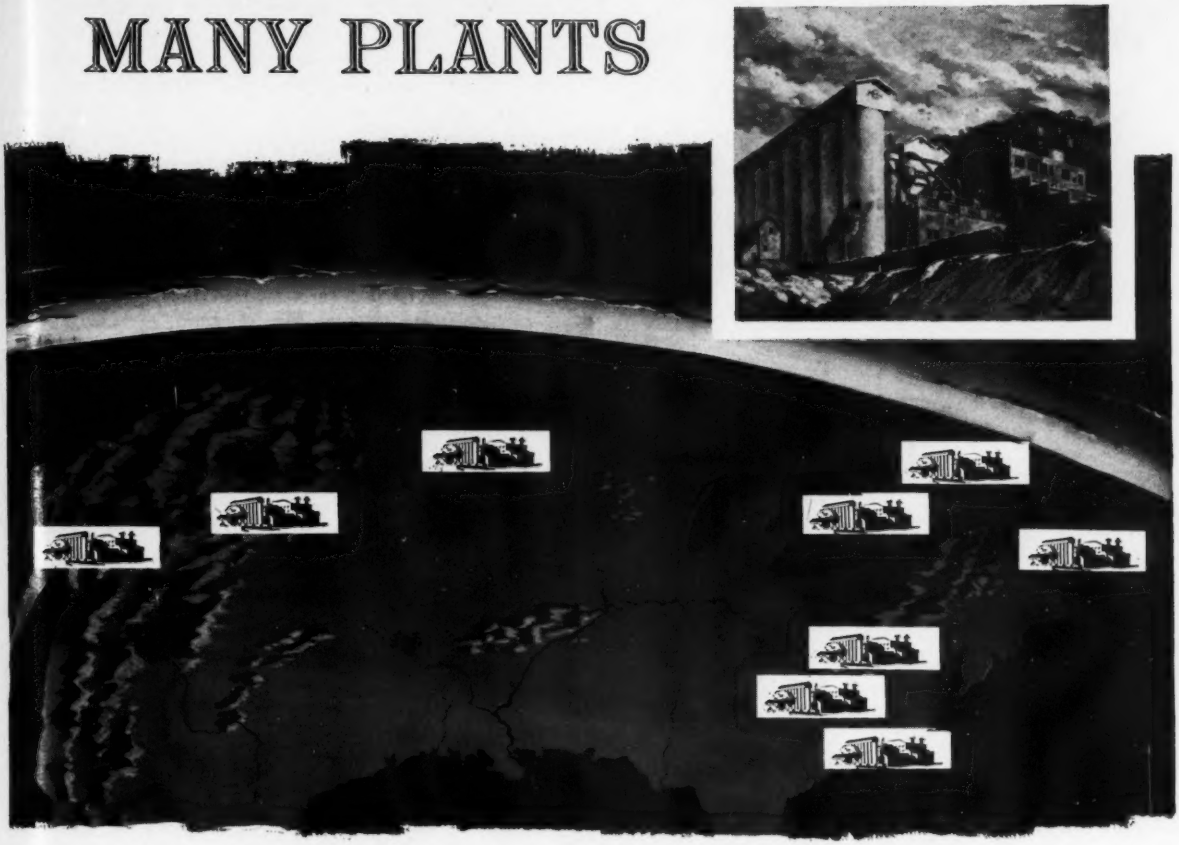
August 28:
- S. W. Barber. Dispersion of Acoustic Waves at Low Temperature in Binary Alkali Silica Glass and Its Relation to Other Mechanical Properties.
- R. J. Charles. Effect of Temperature and Atmosphere on the Corrosion Fatigue of Lime Glass.

August 29:
- Summary Discussion; Overflow Papers; Business Meeting.

• Z. A. Sutter has been named comptroller of Glasco Products Company, Chicago, Ill., subsidiary of Owens-Illinois Glass Company. In announcing the appointment, Harlan Hobbs, Glasco president, stated that the addition of Mr. Sutter to his staff follows the development and expansion of several new Glasco lines and customer service procedures in the public health and hospital fields.

**Another Ingredient of Leadership...**

# MANY PLANTS



## CONSOLIDATED FELDSPAR'S *nine plants provide you security of supply and fast, dependable, low cost deliveries*

You get, *exclusively from Consolidated Feldspar*, the extra margin of safety and the comfortable confidence of security of supply that are assured by nine plants producing *Feldspar, Nepheline Syenite* and *Aplite*.

Over a period of many years, *Consolidated Feldspar* has developed new mining properties and built new plants, always in advance of urgent market demands, to provide the glass and ceramic industries the assurance of ample producing capacity. Today, nine mills are conveniently located to provide prompt deliveries of the material and the grade you want, in whatever tonnages you need, anytime.

*Consolidated Feldspar* is the one strong producing organization with multiple plants, vast ore reserves, a full range of materials and grades, large capacities and product quality rigidly maintained by extensive research and control laboratory facilities.

| FELDSPAR | *Blue Mountain* | APLITE |
|---|---|---|
| *All types and grades* | NEPHELINE SYENITE | *Regular and Treated* |

International MINERALS & CHEMICALS

**CONSOLIDATED FELDSPAR**

DEPARTMENT

INTERNATIONAL MINERALS & CHEMICAL CORPORATION, 20 NORTH WACKER DRIVE, CHICAGO 6

EXCLUSIVE SALES AGENTS FOR CLINCHFIELD SAND AND FELDSPAR CORPORATION, BEDFORD, VIRGINIA

AFFILIATE: CANADIAN FLINT & SPAR DEPT., 77 METCALFE ST., OTTAWA, CANADA

### HKP REFRACTORIES DIVISION APPOINTS WILLIAMS AND WILEY

Dan D. Williams has been appointed assistant general sales manager, and Curt K. Wiley named Pittsburgh district sales manager, Refractories Division, H. K. Porter Company, Inc., according to an announcement by Alan R. Eakins, general sales manager of the division.

Mr. Williams was previously with E. J. Lavino and Company in various sales positions since 1950. He is experienced in the technical sale and service of basic refractories. A graduate of Princeton University, Mr. Williams was employed as a sales engineer for Bonney Forge and Tool Works, Allentown, Pa. from 1948 to 1950.

Mr. Wiley was formerly president of the Gem Clay Forming Company, Sebring, Ohio. He served in the U. S. Naval Reserve as a Lieutenant Commander in World War II. He was graduated from Mt. Union College with a B. A. degree and from Western Reserve University School of Law with an LLB degree.

### ALFRED U. RECEIVES TWO GRANTS

Two grants totaling $8500 have been received by State University of New York College of Ceramics at Alfred University. President M. Ellis Drake said the grants consist of $6500 from the Orton Ceramic Foundation of Columbus, Ohio, and $2000 from the Continental Can Company.

The grant from the Orton Foundation will be used to purchase new X-ray equipment for the College of Ceramics. It will be available for research and for general use by graduate and undergraduate students.

The $2000 from Continental Can Company is unrestricted and may be applied to any phase of the ceramic program.

Dean John McMahon of the College of Ceramics, in expressing his appreciation to the two donors, thanked them for their generosity and their interest in Alfred University and the College of Ceramics.

### NEW POSTS ASSIGNED AT OWENS-ILLINOIS

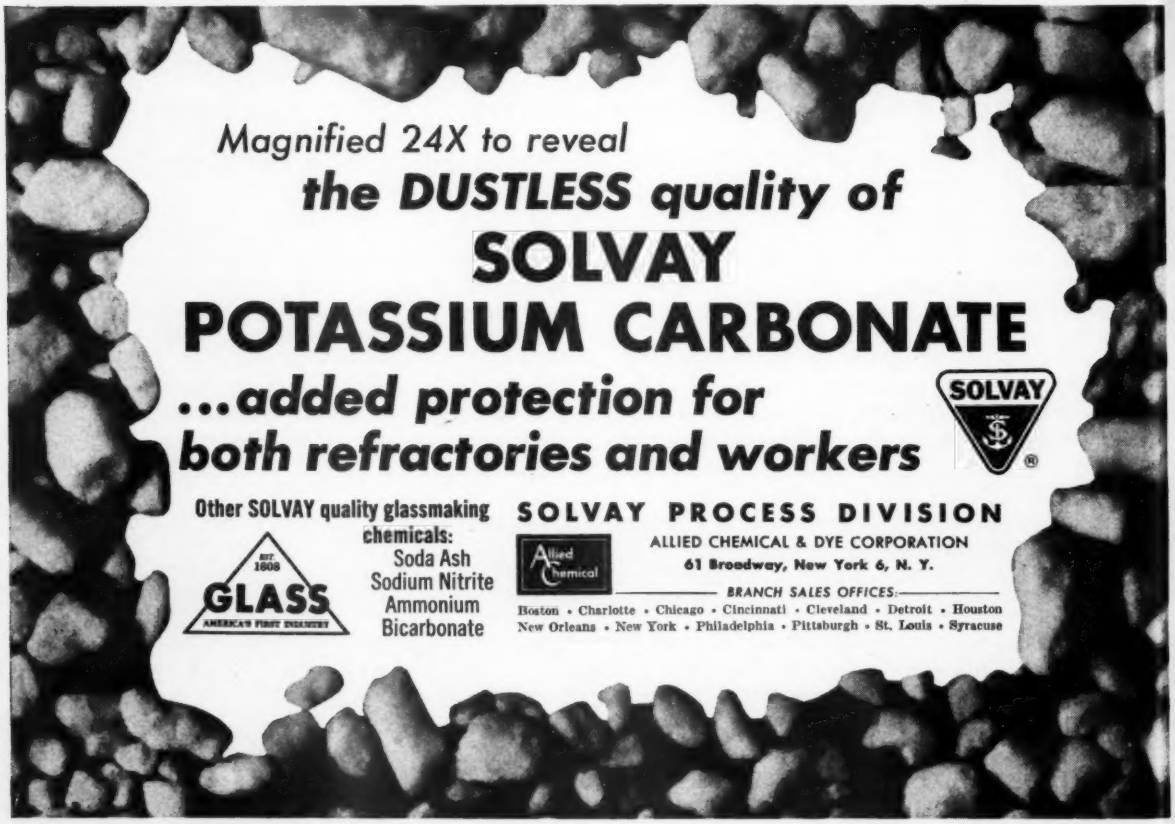
Three Toledoans were recently given important new posts in Owens-Illinois Glass Company by the O-I board of directors at its quarterly meeting in Toledo.

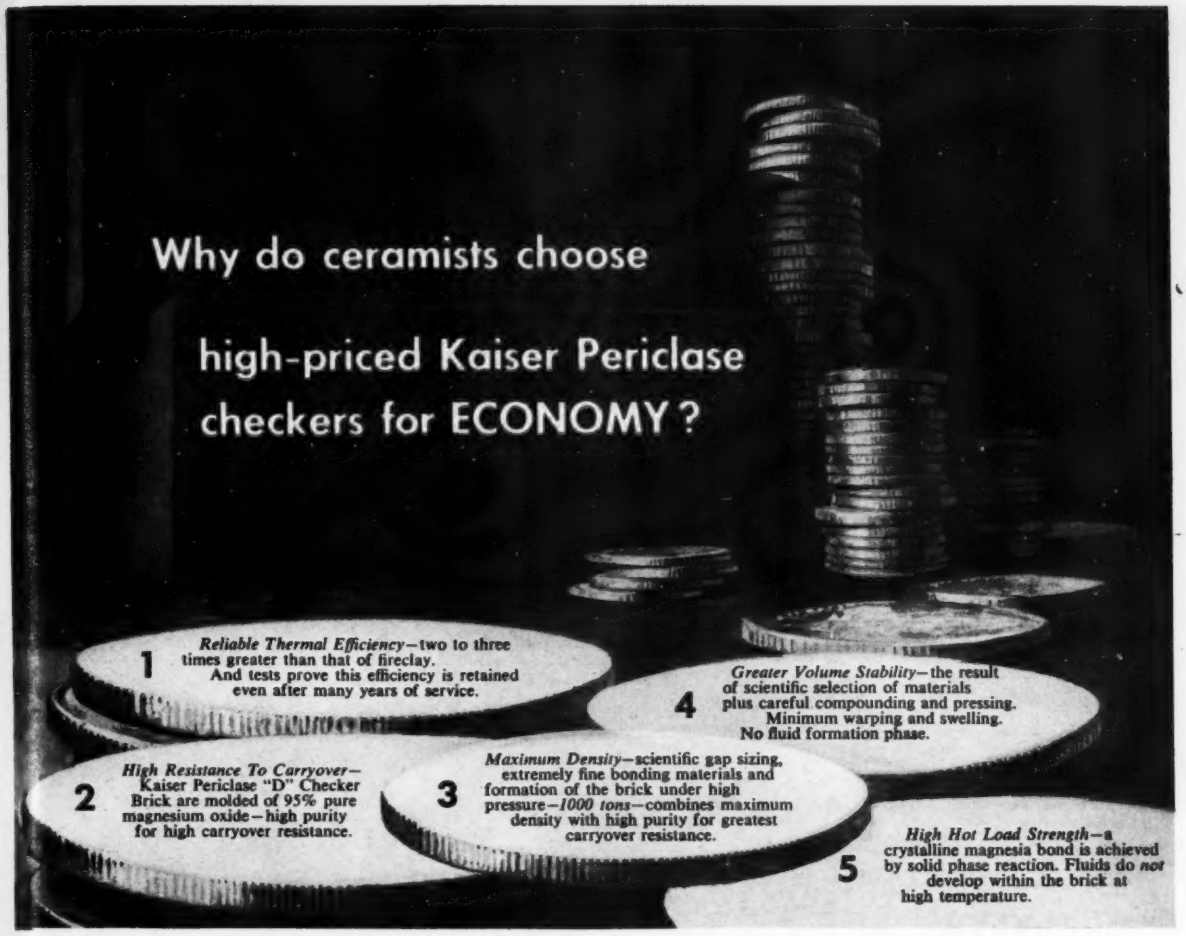
Palmer W. Hancock, vice president since 1956 and comptroller of the Company for eight years before that was named vice president-finance with responsibility for treasury, accounting and administrative areas.

Charles F. Babbs, assistant general counsel, was named secretary of Owens-Illinois. He also will continue as assistant general counsel, a post he has held since 1953.

Earl E. Smith, assistant secretary and assistant treasurer of the Company since 1951, was named treasurer.

Mr. Smith and Mr. Babbs will divide the secretary-treasurer post held for many years by John H. McNerney. Mr. McNerney, who is retiring, has been secretary of O-I since 1926 and its treasurer since 1939.



Magnified 24X to reveal
the DUSTLESS quality of
SOLVAY
POTASSIUM CARBONATE
...added protection for
both refractories and workers
SOLVAY
Other SOLVAY quality glassmaking chemicals:
Soda Ash
Sodium Nitrite
Ammonium Bicarbonate
EST. 1808
GLASS
AMERICA'S FIRST INDUSTRY
SOLVAY PROCESS DIVISION
Allied Chemical
ALLIED CHEMICAL & DYE CORPORATION
61 Broadway, New York 6, N. Y.
BRANCH SALES OFFICES:
Boston • Charlotte • Chicago • Cincinnati • Cleveland • Detroit • Houston
New Orleans • New York • Philadelphia • Pittsburgh • St. Louis • Syracuse


Why do ceramists choose
high-priced Kaiser Periclase
checkers for ECONOMY?
1 Reliable Thermal Efficiency—two to three times greater than that of fireclay. And tests prove this efficiency is retained even after many years of service.
2 High Resistance To Carryover—Kaiser Periclase "D" Checker Brick are molded of 95% pure magnesium oxide—high purity for high carryover resistance.
3 Maximum Density—scientific gap sizing, extremely fine bonding materials and formation of the brick under high pressure—1000 tons—combines maximum density with high purity for greatest carryover resistance.
4 Greater Volume Stability—the result of scientific selection of materials plus careful compounding and pressing. Minimum warping and swelling. No fluid formation phase.
5 High Hot Load Strength—a crystalline magnesia bond is achieved by solid phase reaction. Fluids do not develop within the brick at high temperature.

**Although ceramists** are generally agreed that Kaiser Periclase "D" Brick are the best-performing checker brick available, one additional fact must still be faced: *Kaiser brick are probably the highest-priced checker brick you can buy.*

Where, then, is the economy?

The only possible answer, of course, is that the bricks' performance properties *must make a whopping big difference* in furnace results. They do!

### Thermal Efficiency Saved $82,000 In Fuel

Take for example the first property listed: "Reliable Thermal Efficiency" (the ability to hold heat and conduct heat). Here are figures from an actual comparison:

| | Campaign "A" Fireclay; token use of basic brick | Campaign "B" Extensive use of basic brick |
|---|---|---|
| Life — Operating days | 720 | 1,038 |
| Pull — Total tons of glass melted | 70,348 | 109,423 |
| Average tons of glass per operating day | 97.8 | 105.4 |
| Total tons of glass per square foot of melting area during campaign | 100.6 | 156.3 |
| Square feet of melting area per ton per day | 7.16 | 6.64 |
| Average fuel consumption, cubic feet of gas per ton of glass produced | 10,967 | 8,662 |

The fuel consumption in campaign "A" increased from 9342 cubic feet at the start to a high of 11,600 during the latter part of the campaign (figures from months having same average glass production rates).

In campaign "B," the regenerative cycle was shortened from 20 to 15 minutes to take advantage of the higher thermal efficiency of the basic brick . . . *and gas consumption remained an almost constant 8662 cubic feet throughout the nearly three years of the campaign!*

The plant saved 2305 cubic feet of gas per ton of glass produced as compared to campaign "A"—resulting in a saving of 74.9 cents per ton, or a total saving of $82,000 on fuel over the three-year campaign. Management gives almost full credit to the checker setting.

### Performance Boosts Production, Cuts Down Time

Yet, fuel saving is only part of the story. Huge additional savings and profits can properly be credited to the performance of Kaiser Periclase checkers . . . greater production per square foot of hearth . . . longer campaign life.

*These bricks have consistently served in continuous glass container furnace campaigns that have lasted up to four years —campaigns terminated due to failure of other refractories.*

For supporting data on how the superior characteristics of Kaiser Periclase brick can increase the efficiency of your operation, ask for our booklet, "A Report on a Better Basic Brick for the Glass Industry."

Call or write Kaiser Chemicals Division, Dept. G-8912, Kaiser Aluminum & Chemical Sales, Inc., at any of the Regional Offices listed below:
PITTSBURGH 22, PA. . . . . 3 Gateway Center
HAMMOND, IND. . . . . 518 Calumet Building
OAKLAND 12, CALIF. . . . . 1924 Broadway

KAISER CHEMICALS

PIONEERS IN MODERN BASIC REFRACTORIES

BASIC REFRACTORY BRICK AND RAMMING MATERIALS • DOLOMITE MAGNESIAS • ALUMINA • MAGNESITE • PERICLASE

SEE "MAVERICK" • SUNDAY EVENINGS, ABC-TV NETWORK • CONSULT YOUR LOCAL TV LISTING

## TUMBLER WINS BREWERS' GOLD MEDAL AWARD

The red and white Storz pennant-decorated "Hour Glass" tumbler made by the Bartlett-Collins Company, manufacturers of glass tableware in Sapulpa, Oklahoma, was given the first prize Gold Medal Award for excellence in glass design in 1957 at the sixteenth annual convention and exhibit of the Brewers' Association of America at Chicago.

The "Hour Glass" was designed and manufactured by Bartlett-Collins in their Sapulpa plant. The screened Storz pennant was applied by the Bartlett-Collins decorating department.

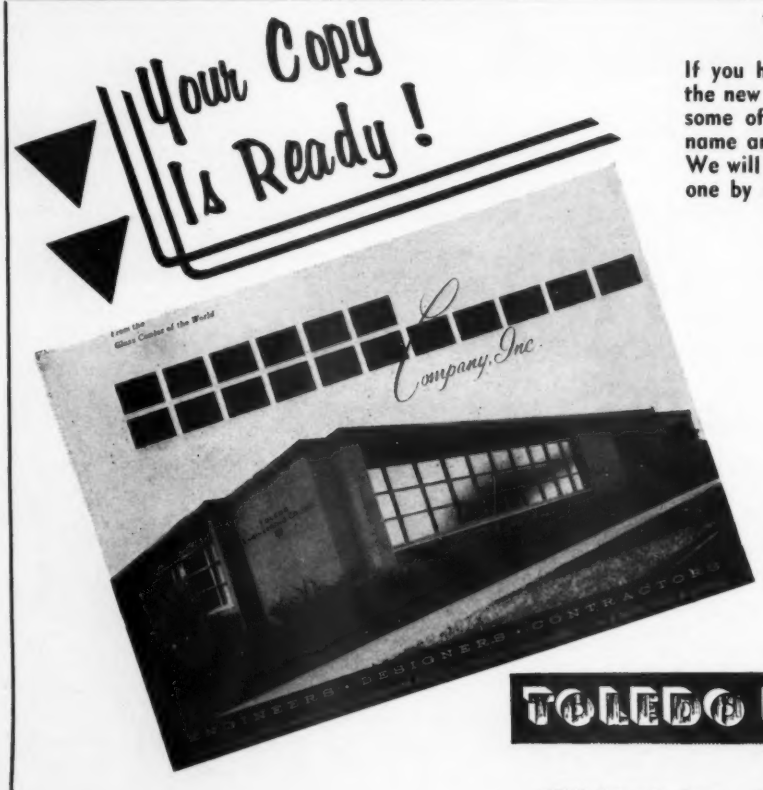
**The Brewers' Association of America Award is shown with the winning tumbler, designed for Storz Brewing Company, Omaha, Neb.**

## AMERICAN GLASSWARE ASSOCIATION ELECTS BOARD OF GOVERNORS

The American Glassware Association has announced elections to its board of governors. The Association's secretary, R. L. Davis, stated that the industry representatives are elected for a two year period.

They are: J. N. McNash, sales manager, Hazel-Atlas Glass Division, Continental Can Company, elected chairman of the board of governors and governor representing Division E, the automatic machine-made glassware division; J. C. Weber, Jr., secretary and sales manager, West Virginia Glass Specialty Company, representing Division H, the handmade glassware division; J. F. Gillinder, president of Gillinder Brothers Company, representing Division M, the illuminating, industrial and scientific glassware division; W. F. Dalzell, president of Fostoria Glass Company, governor-at-large; E. A. Donnan, president of The Federal Glass Company, governor-at-large; and A. M. Turner, vice president and general manager of Libbey Glass Division, Owens-Illinois Glass Corp., alternate governor-at-large.

Those appointed by the respective Divisions to serve as standing alternates to division governors are: C. C. Stein, general sales manager of The Federal Glass Company, standing alternate to the governor of Division E, automatic glassware; R. S. Holt, president of Bryce Brothers Company, standing alternate to the governor of Division H, handmade glassware; and M. T. Gleason, secretary of Rodefer-Gleason Glass Company, standing alternate to the governor of Division M, illuminating, industrial and scientifc glassware.


If you have not already received a copy of the new brochure depicting our facilities and some of our installations, please send your name and title on your company letterhead. We will consider it a privilege to forward you one by return mail.

ENGINEERS
★
DESIGNERS
★
CONTRACTORS

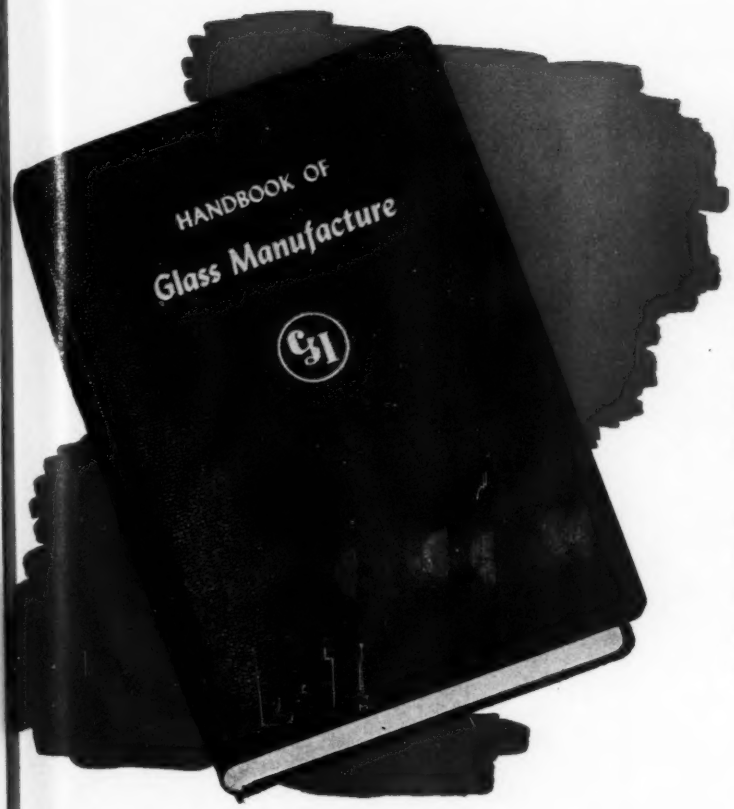
A complete service to all branches of the Glass Industry. We also design special purpose melting furnaces for the Chemical industry and design and construct complete lime plants, providing equipment when desired.

TOLEDO ENGINEERING Company

3003 Sylvania Ave. — GReenwood 5-1529 — Toledo 13, Ohio

# *Again available*

## Handbook of Glass Manufacture




### *Second Printing*

Just three years ago the *new* HANDBOOK OF GLASS MANUFACTURE was offered to the glass manufacturing industry and eighteen months after publication the entire edition was sold out.

Without interruption the demand for copies of the Handbook has continued and it is for this reason that we decided to bring out a second edition of the book. This second printing, identical in content, format and binding, is now available.

The continued demand for the HANDBOOK OF GLASS MANUFACTURE proves that it has filled an important role as a practical working tool for *glass plant executives, research heads, laboratory technicians, engineers and technologists.*

Send for your personal copy Now!

GJ

**The Glass Industry**
**55 West 42nd Street, New York 36, New York**

Date.....

Enclosed please find remittance in the amount of $..... to cover the cost of ..... copies of the HANDBOOK OF GLASS MANUFACTURE. Single copy price, $11.50. Order for 5 or more copies, 10% discount. Add Shipping and Insurance charges, domestic 60¢; foreign 90¢. Foreign remittance in U.S dollars.

NAME.....

COMPANY.....

STREET..... CITY..... STATE.....